Kereszténvi István, Babos Katalin, Bohács György, Siklósi Tamás

ISSN 0350-350X
GOMABN 52, 4, 296-304
Izvorni znanstveni rad / Original scientific paper

DEVELOPMENT OF REFINERY CO_2 CAPTURE BY MICROALGAE

Abstract

As a significant emitter of carbon-dioxide in the region MOL Hungarian Oil & Gas Plc. has launched an extensive research program associated with carbon capture and utilization. Research is focused on the utilization of carbon dioxide as a feedstock for biological processes such as greenhouse growing and microalgae cultivation for further industrial applications. For the development of microalgae related technologies MOL Downstream Development has established collaboration with several scientific institutions to screen for the most productive microalgal strains, to further increase their productivity by bioengineering, and to develop scalable technologies for the cultivation, separation and processing of microalgae.

The potential of microalgae resides in their increased growth rates and superior lipid content compared to other plants such as rapeseed. An ideal application would therefore be the extraction of these lipids and their processing to next generation biofuels. Based on experiments performed in our outdoor photobioreactors the yearly production of 60-80 t/ha dry algal biomass and the recovery of approximately 20 t/ha algal oil are estimated.

However, the aquatic nature of these microorganisms requires cost intensive pretreatment technologies to be applied prior to extraction which offset the improved yield. As opposed to extraction biogas production does not require expensive pretreatment to be applied (5 wt% dry matter content is sufficient), therefore it could be a better alternative for processing microalgae. Based on the current status of research the feasibility of extraction and biogas production has been thoroughly studied and assessed.

Key words: *refinery, microalgae, CO_2 capture, photobioreactor*

RAZVOJ POSTUPKA UKLANJANJA RAFINERIJSKOG CO_2 MIKROALGAMA

Sažetak

S obzirom na ispuštanje značajnih količina ugljikovog dioksida, čak i regionalno gledano, MOL d.d. je pokrenuo opsežan istraživački program hvatanja i korištenja ugljika. Istraživanje je usmjereno na korištenje ugljikovog dioksida kao sirovine za biološke procese kao što su staklenički uzgoj i uzgoj mikroalga za daljnje industrijske primjene. Radi razvoja tehnologija povezanih s mikroalgama, MOL Downstream Developement je uspostavio suradnju s nekoliko znanstvenih institucija kako bi se pronašli najproduktivniji sojevi mikroalgi, kako bi se bio-inženjeringom dodatno povećala njihova produktivnost, te se te tehnologije uzgoja, odvajanja i procesa na temelju rada mikroalga prenijele na veće razmjere.

Potencijal mikroalga počiva u njihovim velikim brzinama rasta i značajno većem sadržaju lipida u odnosu na druge biljke, npr. uljanu repicu. Idealna primjena bi stoga bila izdvajanje tih lipida i njihova prerada u sljedeću generaciju biogoriva. Na temelju eksperimenata provedenih u otvorenim fotobioreaktorima procjenjuje se godišnja proizvodnja od 60 do 80 t / ha suhe biomase alga i dobivanje oko 20 t / ha goriva iz alga.

Međutim, vodena priroda tih mikroorganizama zahtijeva skupe tehnologije predobrade koji se moraju provesti prije ekstrakcije, a koje se financijski opravdavaju povećanim prinosom na kraju. Za razliku od ekstrakcije, proizvodnja bioplina ne zahtijeva skupu predobradu (dovoljan je sadržaj suhe tvari od 5 % mas). Stoga bi to mogla biti bolja alternativa za procese pomoću mikroalga. Izvedivost ekstrakcije i proizvodnje bioplina su temeljito proučene i ocijenjene na temelju trenutačnog stanja istraživanja.

Ključne riječi: *rafinerija nafte, mikroalge, CO_2 hvatanje, fotobioreaktor*

Introduction

By the end of the 20th and the beginning of the 21st century, fighting global warming has become one of the major topics throughout the world. It is believed that global warming is mainly the result of human activity, particularly the increasing emission of greenhouse gases into the atmosphere. As among the greenhouse gases carbon dioxide is considered to be the most responsible for global warming, several research & development & investigation projects associated with carbon capture and utilization have been launched worldwide in order to reduce carbon dioxide (CO_2) emissions, and possibly utilize carbon dioxide as a feedstock for other technologies. These technologies may include the synthesis of organic chemicals, such as methanol, urea, salicylic acid, etc., other chemical processes like supercritical extraction, or biotechnologies, where carbon dioxide would be the feedstock of an autotrophic organism (Li et al., 2006).

While there are lots of possibilities, most of them are not yet economical on the commercial scale, hence R&D&I are focused on improving these technologies to become commercially viable.

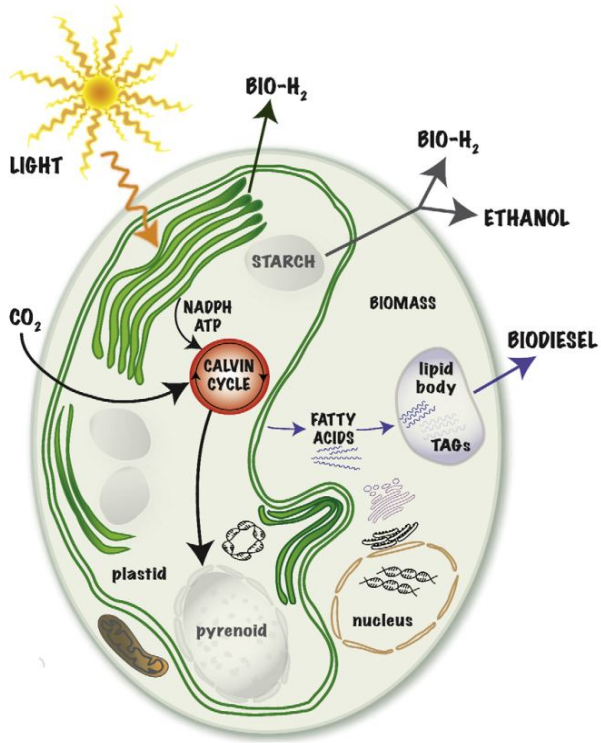

Figure 1: Metabolic pathways of microalgae related to biofuel and biohydrogen production (Beer et al., 2009)

Algae are a large group of unicellular (microalgae) and multicellular (macroalgae, seaweeds) organisms usually present in aquatic environments in planktonic form, or in symbiosis with other organisms (coral reefs, sea sponges). Algae are typically autotrophic organisms, and use carbon dioxide as their carbon source, but some are also capable of heterotrophic metabolism of organic substances (Chen et al., 2011). Their advantage in carbon capture lies in increased growth rates compared to other plants, and therefore potentially higher productivities per hectare (Chisti, 2007), while not competing for land with food agriculture.

Another advantage of algae is the enormous variety of organic compounds that can be produced from them varying from biofuels, fertilizers, and animal feeds, to food supplements, cosmetics and even pharmaceuticals.

Energetic related applications of microalgae include hydrogen (Miura et al., 1995), methane (Zamalloa et al., 2011), ethanol (John et al., 2011), or biodiesel (Chisti, 2007) production. A sketch of the various microalgal metabolic pathways related to biogas and biofuel production is demonstrated in Figure 1. As demonstrated in the figure, microalgae are organisms capable of producing hydrogen through photosynthesis, and synthesize starch and lipids as carbon storage materials, which can be converted into biofuels. While some technologies are based around the exploitation of these metabolic pathways, and the extraction of these materials from the microalgal cells, others use the entire cell and convert cell biomass to value added products. These conversions are usually either biochemical or thermochemical conversions, both of which have been studied extensively (Brennan & Owende, 2010).

Due to their great potential transportation biofuels production from microalgae (and cyanobacteria) has recently gained much attention, with over a dozen major and hundreds of smaller projects all around the world. Major participants are companies like ExxonMobil (teamed up with Synthetic Genomics), Sapphire Energy, Algenol Biofuels, Aurora Algae, Eni, SolixBiosystems, Cellana and Joule Unlimited, but the European Commission FP7 Programme is also extensively funding research related to microalgae (Benemann et al., 2011). The most committed company is inarguably ExxonMobil, which will invest 600 million USD to develop genetically modified strains capable of excreting hydrocarbons, but other companies have also come up with innovative ideas like Algenol, which claims to have developed a strain capable of excreting ethanol. Although a lot of these projects are centered around genetic engineering of microalgae in order to enhance a specific metabolic pathway, research on cultivation, separation and processing are also important, as so far none of the developed technologies has proven to be significantly better than the rest in terms of overall efficiency.

In this paper research activity at MOL Downstream Development concerning microalgae related technologies is presented along with a brief economic analysis of the current cost of microalgal carbon capture based on local experimental results.

Tools for strain selection, genetic engineering and cultivation

In order to enhance overall productivity several microalgae strains were isolated from their natural environments and screened for superior growth rates at both higher and lower temperatures. Screening was carried out in 500 ml flasks, using BM2 synthetic growth medium, 21±1 ^{o}C for higher and 16±1 ^{o}C for lower temperatures, 24 hour illumination (5000 lux, “daylight” neon lights), and 1 l/min aeration with 2.5 v/v % CO_2 concentration for 4 days. The most promising strains were then subjected to random mutagenesis, which was performed by adding 10, 20, 40, 80 mM EMS (ethyl methanesulfonate) to the flasks.

Samples were incubated in the dark for two days, and then grown in 24 hour illumination for two weeks. After two weeks fresh growth media were inoculated with these samples and screened for increased productivity.

The effect of different cultivation parameters (CO_2 concentration, pH, composition of the growth medium) was studied in laboratory photobioreactors, which consisted of several bubble column reactors. Each reactor contained 2 dm^3 algae broth, and had a surface area of 0.1 m^2. Reactors were illuminated by artificial lights (Sylvania aqua star, 18 W), using a day/night cycle of 16/8 h in order to simulate natural diurnal cycles. Air from the compressor was supplied constantly, but carbon dioxide from the cylinder was coupled to the illumination of the reactors and thus followed the same day/night cycle. Experiments usually lasted seven days. On the first day of an experiment, algae from the previous experiment were harvested, and a certain portion of the harvested algae was used for inoculating the reactors.

Figure 2: Outdoor flat-panel bioreactors

Apart from laboratory experiments outdoor pilot-scale experiments were performed as well in order to study the effect of weather and to assess the feasibility of the current cultivation system. Experiments were conducted in closed flat-panel photo-bioreactors which operated in batch mode. Each panel consisted of two separate compartments of approximately 50-100 dm^3 depending on the thickness of the panel and the illuminated surface area of each bag was 2 m^2. The growth medium was semi-synthetic, and was produced by mixing several inorganic salts with treated wastewater from the wastewater treatment plant.

Nitrogen was supplied by sour water generated at the Hydrodesulphurization plant of the Danube Refinery. This wastewater usually contains approximately 15 g/dm^3 ammonium-ions, 20 g/dm^3 sulfide-ions and has pH of 12-13. As sulfide-ions are toxic to aerobic organisms (National Research Council, 1979), they were removed by acid stripping, which lowered the sulfide content to 0.1 g/dm^3, and the pH to 4.5. 4 dm^3 of treated sour water was added to each m^3 of growth medium, and no other form of nitrogen was supplied, thus resulting in approximately 60 mg/dm^3 ammonium-nitrogen concentrations. The final pH of the growth medium was from 7 to 8. During cultivation carbonated air was introduced into the reactors in order to supply algae with carbon dioxide, and to provide sufficient mixing of the culture medium. While air was introduced 24 hours a day, carbon dioxide was mixed into the air only during daytime, from 7 a.m. to 8 p.m., and was switched on or off manually by the operators. During the summer cooling the reactors was essential in order to avoid culture death due to overheating. Therefore perforated pipes were installed horizontally above each panel, through which water was automatically introduced to the outer surface of the bags, whenever the temperature of the growth medium exceeded 25 ^{o}C. Experiments usually lasted 5-10 days, after which algae were harvested and concentrated by sedimentation or used for inoculation. Sediments were collected for further experiments.

Tools for separation and processing

As the water content of the harvested microalgae broth is over 99 %, the suspension must be concentrated before processing. Among the various alternatives (Brennan & Owende, 2010) sedimentation and membrane separation were studied due to their low cost (sedimentation) and high efficiency (membrane separation). For the sedimentation experiments, samples were taken from the reactors, supplemented with various chemicals (NaOH, $Fe_2(SO_4)_3$, Poly-DADMAC cationic flocculant) to induce flocculation and allowed to settle. Membrane separation experiments were performed with an UF membrane with 0.4 μm average pore size in a Zenon ZW-10 tubular laboratory membrane module with 289 m^2/m^3 specific surface area. During the separation air was introduced into the membrane tank in order to provide sufficient mixing of the microalgae suspension and to clean the membrane surface, thereby delaying membrane fouling. Permeate was collected with a permeate pump, which automatically performed backwash as well, 600 s filtration was followed by 60 s backwash. After harvesting and concentration, the resulting microalgal biomass was processed by either lipid extraction or anaerobic fermentation. Lipid extraction was performed using 1:2 chloroform/methanol (Bligh-Dyer method), acetone, n-hexane, or industrial gasoline to determine the total lipid content of the biomass and to compare the performance of some industrial solvents and industrial gasoline.
While lipid extraction seems to be a plausible solution for processing microalgal biomass, a recent study concluded that if cell lipid content does not exceed 40 % dry weight, then anaerobic digestion of the whole biomass appears to be better suited from an energy balance point of view (Sialve et al. 2009).

Therefore, laboratory experiments were conducted to assess the potential of biogas production as well. Anaerobic fermentation was performed at two temperatures, 30 ^oC and 40 ^oC, with or without ultrasonic pretreatment (which is commonly used prior to anaerobic digestion in order to disrupt cells and thereby improve biogas yield). The microalgal suspension was inoculated with 640 ml anaerobic sludge from a nearby biogas facility and the amount of produced biogas was monitored for 40 days.

Results

Growth rates at 16 ^oC were approximately half of the growth rates at 21 ^oC in most cases, and mutagenesis usually decreased growth rates for both higher and lower temperatures. However, a few strains exhibited growth rates as much as 30 % higher than the control samples. These strains are currently maintained for further experiments (MOL DS Development 2011).

Results of laboratory experiments on microalgae cultivation confirm the importance of maintaining proper pH levels, as growth rates at pH 5.5 were approximately 15-30 % lower than growth rates at pH 7 and even lower at pH 8.5. This information is very important as the consumption of some substrates (e.g. NH_4^+, NO_3^-) is not pH neutral and can seriously effect productivity and operation stability as it was experienced in case of outdoor pilot-scale experiments. Although the effect of altered carbon dioxide addition between 1 and 5 v/v % was not significant, further experiments concluded that proper adjustment of carbon dioxide concentrations could be a cheap way of maintaining optimal pH levels throughout the cultivation. As a result of successful strain selection, strain improvement and optimization of the culturing technique the oil content of dry algal biomass increased from 15-17 % to 35 % (MOL DS Development 2011).

Last year the best daily productivity with the outdoor flat-panel photobioreactors was 150 $mg/dm^3/d$ (MOL DS Development 2011). Although this performance could not be maintained for a long time, it was probably due to several malfunctions experienced throughout the year. If this productivity could be maintained for 300 days a year in the future, that would equal approximately 40-50 t/ha/y productivity. Based on the average elemental composition of microalgae (Chisti, 2007), the consumption of approximately 1.88 g carbon dioxide is required to yield 1 g of microalgae, therefore the production of 40-50 t/ha/y microalgae would utilize 75-95 t/ha/y carbon dioxide. The theoretical maximum productivity in our climate is 80-120 t/ha/y (Tredici, 2010), which would mean the utilization 150-225 t/ha/y carbon dioxide.

The addition of NaOH to the growth medium successfully induced flocculation. Rising the pH above 11 resulted in an increase of five orders of magnitude from 10^{-7} m/s to 10^{-2} m/s in the settling rate of microalgal flocks (MOL DS Development 2011). However, such alkalinity should be avoided because it can adversely affect the further processing of the separated algal biomass.

Lipids extracted by conventional solvents were between 15-30 % of the dry algal biomass, while industrial gasoline proved to be less efficient, resulting in only 6-8 %. The composition of the extract was the same however. After ultrasonic pretreatment and without sonication, anaerobic fermentations at 30 ^{o}C resulted in 300 and 200 cm^3 biogas/g microalgae respectively, while fermentations at 40 ^{o}C resulted in 25-100 % higher yields. Methane content of the biogas from 30 ^{o}C fermentations was 58 % (MOL DS Development 2011).

Economics

Estimating an theoretical 120 t/ha/y microalgal productivity the cost of microalgae production in flat-panel photobioreactors would be approximately 1.5 €/kg algae, and the cost of CO_2 utilization would be approximately 0.8 €/kg CO_2. These calculations take into account both the CAPEX and OPEX of a flat-panel system for an estimated 10 years of operation.

As the commercial value of microalgal biomass is approximately 0.10-0.15 €/kg dry biomass based on its energy content, these production costs are unacceptably high for industrial scale carbon capture. However, almost 80 % of the total costs come from the CAPEX of the flat-panel photobioreactors, therefore these costs could be reduced with a much cheaper cultivation system (MOL DS Development 2011). The development of such system is in progress at MOL Development organization.

Conclusion

Among the various alternatives to carbon capture and utilization microalgae cultivation is currently one of the less mature and more expensive alternatives. In order to improve productivity, continuous strain selection and strain improvement is crucial, as well as the development of a cheap and reliable cultivation system. Effective separation and processing technologies need to be developed as well in order to increase the value of this otherwise worthless feedstock. However, the potential of microalgae for CO_2 utilization is enormous, and it is hard to confirm or deny if we can exploit this potential in the future or not. Our challenge for the years to come is to advance in all fields of this technology from strain improvement to biomass processing and significantly reduce production costs.

References

1. Benemann, J., Woertz, I., Lundquist, T. (2011): Life Cycle Analysis for Microalgae Oil Production. 20th World Petroleum Congress, Doha 2011, forum 16: Biofuels and biomass: feedstock options life cycle analysis.
2. 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.

3. Chen, C.-Y., Yeh, K.-L., Aiyah, R., Lee, D. J., Chang, J.-S. (2011): Cultivation, photobioreactor design and harvesting of microalgae for biodiesel production: A critical review. BioresourceTechnology; 102: 71-81.
4. Chisti, Y. (2007): Biodiesel from microalgae. Biotechnology Advances; 25: 294-306.
5. John, R.P., Anisha, G.S., Nampoothiri, K.M., Pandey, A. (2011): Micro and macroalgal biomass: A renewable source for bioethanol. Bioresource Technology; 102: 186-193.
6. Li, Y., Markley, B., Mohan, A. R., Rodriguez-Santiago, V., Thompson, D., Niekerk, D. V. (2006): Utilization of Carbon Dioxide from Coal-Fired Power Plant for the Production of Value Added Products. Design Engineering of Energy and Geo-Environmental Systems Course (EGEE 580).
7. Miura Y., Akano, T., Fukatsu, K., Miyasaka, H., Mizoguchi, T., Yagi, K., Maeda, I., Ikuta, Y., Matsumoto, H. (1995): Hydrogen Production by Photosynthetic Microorganisms. Energy Conversion and Management; 36 (6-9): 903-906.
8. MOL DS Development (2011): CO_2 capture of refinery fluegas by micoalgae. Final Report, 2011. MOL Hungarian Oil and Gas Plc Downstream Development, Százhalombatta, 1-10 pp.
9. National Research Council, Division of Medical Science, Subcommittee on Hydrogen Sulfide, 1979. Hydrogensulfide, University Press, Baltimore, 183 pp.
10. Oren, A., Padan, E., Malkin, S. (1979): Sulfideinhibition of the photosystem II in cyanobacteria (blue-green algae) and tobacco chloroplasts. Biochimica et Biophysica (BBA) – Bioenergetics; 546(2, 9): 270-279.
11. Sialve, B., Bernet, N., Bernard, O. (2009): Anaerobic digestion of microalgaeas a necessary step to make microalgal biodiesel sustainable. Biotechnology Advances; 27(4): 409-416.
12. Tredici M.R. (2010): Photobiology of microalgae masscultures: understanding the tools for the next green revolution. Biofuels; 1: 143-162.
13. Zamalloa, C., Vulsteke, E., Albrecht, J., Verstraete, W. (2011): The techno-economic potential of renewable energy through the anaerobic digestion of microalgae. BioresourceTechnology; 102: 1149-1158.

Authors
Kereszténvi István, Babos Katalin, Bohács György, Siklósi Tamás
MOL Hungarian Oil & Gas Plc., Downstream Development

Received
9.10.2012.

Accepted
07.2.2013.