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Short communication

Biorefineries of energy products

[Biorrefinerías de productos energéticos]

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Abstract

Algal biotechnology represents a very versatile platform for environmental applications, contributing to heavy metal removal, organic matter stabilization and nutrient valorization from wastewaters, carbon dioxide capture and sustainable biofuel production. Biodiesel, biohydrogen, biogas and bioethanol constitute the main energy vectors obtained from microalgae. This short communication reviews the potential of microalgae for biofuel production.

Resumen

La biotecnología de las algas representa una plataforma muy versátil para las aplicaciones medioambientales, contribuyendo a la eliminación de metales pesados, la estabilización de la materia orgánica y la valorización de los nutrientes de las aguas residuales, la captura de dióxido de carbono y la producción sostenible de bio-combustibles. El biodiésel, el biohidrógeno, el biogás y el bioetanol constituyen los principales vectores energéticos obtenidos a partir de las microalgas. Esta breve comunicación revisa el potencial de las microalgas para la producción de biocombustibles.

Microalgal Biorefineries

Under nutrient starvation and excess of CO_2 and light, some microalgae can store lipids (10- 80% on a dry weight basis) as energy source, which represents a valuable feedstock for the production of biodiesel (with an average calorific value of 35.8 Kg g^{-1}). Microalgal triglycerides need to be extracted from the cell to be further trans-esterified catalytically using methanol, with the concomitant production of biodiesel and glycerol (as a byproduct). The interest in microalgae biodiesel boomed in 2007 in a global context of rising oil prices and concern about climate change. Unfortunately, the high cost of microalgae cultivation (4-10 € kg^{-1}) jeopardized the widespread production of algal biodiesel (Peng *et al.*, 2020).

Biohydrogen is the gaseous fuel with the highest calorific value (138 KJ g^{-1}) and the lowest CO_2 footprint, although entails technical problems during storage, high explosion risks and low production rates in microalgal photobioreactors. Biohydrogen can be produced via direct biophotolysis or indirect biophotolysis, but the maximum reported production rates are typically lower (0.07-0.36 mmol H_2 L^{-1} h^{-1}) than those achieved during dark fermentation of organic substrates (64-76 mmol H_2 L^{-1} h^{-1}) (Buitrón *et al.*, 2017).

Microalgae can be used as a feedstock for the production of methane via anaerobic digestion (55 KJ g CH_4^{-1}), with the first studies dating back to 1950s in California using the algal biomass generated from domestic wastewater treatment (Golueke *et al.,* 1957). The methane productivity yields of microalgae typically range from 0.09 to 0.45 LCH_4 g VS^{-1}, and depend on the microalgal species and growth conditions, which ultimately determine the Redox state and biodegradability of the carbon present in the biomass. The generation of biogas from residual algal biomass is conducted in anaerobic digesters engineered with internal gas or liquid recirculation, or mechanical agitation, in order to provide the required mixing between the algal substrate and the anaerobic microbial community. Substrates to inoculum ratios of 0.5 were shown optimal for the determination of the biochemical methane potential in batch tests, with ratios over 3 inducing inhibition of the anaerobic community (Alzate *et al.*, 2012).

The development of algal biorefineries for bioenergy production can entail an initial extraction of the algal lipid for biodiesel production, and the further digestion of the lipid-exhausted biomass. This lipid-free biomass supports similar methane yields but significantly faster kinetics due to the partial disruption of cell integrity during lipid extraction (Alzate *et al.,* 2014). On the other hand, the presence in the algal cell wall of recalcitrant compounds has been shown to typically hinder microalgae biodegradability, which requires the implementation of biomass pretreatments such as chemical, thermal, steam explosion, microwave, ultrasound, and enzymatic pretreatments.

Table 1 shows the main algal pretreatments along with their key operational parameters, enhancement potential and their pro and cons. Among the pretreatments reported in literature, thermal and steam explosion pretreatments have shown the largest microalgal biodegradability enhancements, while ultrasound pretreatments typically require more energy than the chemical energy contained in the target biomass.

This biogas can be upgraded to biomethane in order to be used as a substitute of natural gas in natural gas grids or as a gas fuel in vehicles. Membrane-based separation is currently the commercial technology with the largest increases in market share in the past 10 years (WBA, 2019). Hence, membrane technology, which consists of the selective permeation of biogas pollutants such as CO_2 and H_2S through membranes, is a competitive and attractive alternative to conventional upgrading technologies due to its decreasing energy consumption (brought about by the rapid advances in material science), simple and compact engineered modules and small footprint. Although the number of commercially operated plants is still limited, membrane technology is currently undergoing rapid development thanks to the use of new polymer materials with promising properties and enhanced performance and is set to play an increasingly important role in reducing environmental impact and cost of industrial biogas upgrading (Awe *et al.,* 2017).

Among biological biogas upgrading technologies, photosynthetic biogas purification with microalgae represents the only biotechnology capable of simultaneously removing CO_2 and H_2S from biogas, while fixing the nutrients present in the digestate in the form of biomass. Photosynthetic biogas upgrading is based on the combined action of alkaliphilic microalgae and bacteria prior transfer of the main contaminants of biogas into the cultivation broth (CO_2, H_2S, NH_3).

Table 1. Pre-treatments enhancing the anaerobic biodegradability of microalgae.

Pre-treatment	Operational parameters	Anaerobic biodegradability Enhancement	Advantages	Disadvantages
Thermal hydrolysis	Temperature; HRT	++	Lower energy demand; Easy scalability	High HRT
Steam explosion	Temperature; Pressure HRT	+++	Short HRT Easy scalability	High energy demand; High investment cost
Microwave	Power; HRT	++	Less risk of byproduct formation	High electricity demand; Easy scalability
Ultrasound	Energy input; HRT	+	Easy scalability	High electricity demand
Chemical (Acid/Alkaline)	Reagent dose; HRT	+	Low energy demand	Chemical contamination; Risk of formation of inhibitors; High operating cost
Enzymatic	Enzyme dose; HRT pH, temperature	+	Low energy demand	High operating cost, Need for sterile conditions

HRT- Hydraulic Retention Time.

Solar energy drives the photosynthetic assimilation of the CO_2 present in biogas into algal biomass, with the concomitant production of O_2 (~1.5-1.9 g O_2 g CO_2fixed^{-1}). This oxygen is used *in-situ* by chemolithotrophic bacteria to oxidize H_2S to SO_4^{2-}, and NH_3 to NO_3^- (Figure 1). The process is typically carried out at high pH (Rodero *et al*., 2020) in order to improve the mass transfer of the main biogas pollutants (i.e, CO_2 and H_2S). The nutrients and water required to support the growth of microalgae and bacteria can be obtained from the digestate produced in the anaerobic digester, which partially mitigates the eutrophication potential of these high-strength effluents. Methane concentrations over 95 % with CO_2 concentrations below 2% and a complete depletion of H_2S have been recorded in pilot and demo scale photobioreactors using this technology (Marín *et al.*, 2021).

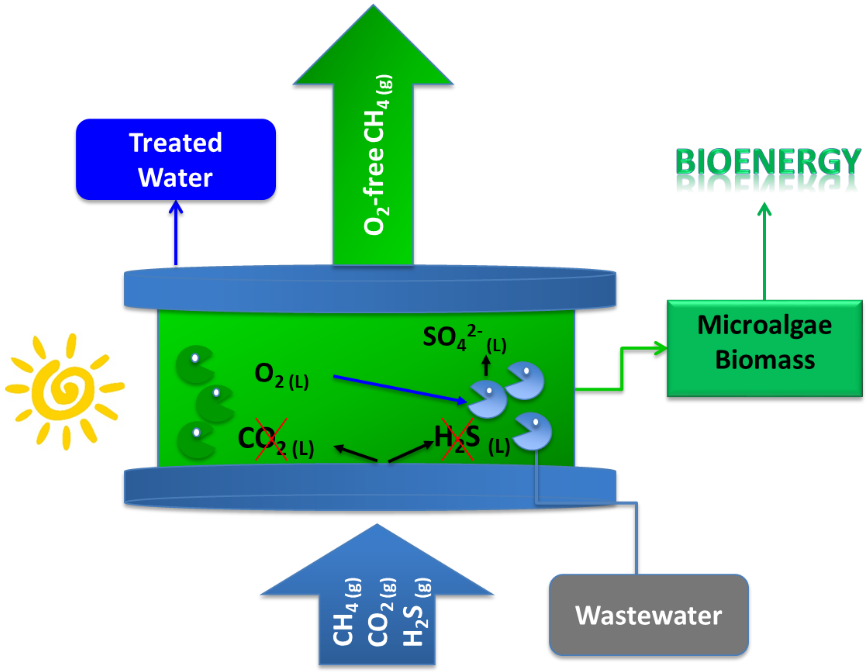

Figure 1. Fundamentals of photosynthetic biogas upgrading.

Bioethanol, with a calorific value of 30 KJ g^{-1}, can be obtained via fermentation of the sugars contained in microalgae. The carbohydrate content of microalgae, which can reach levels ranging from 16.4% to 60%, is extracted via cell disruption using enzymatic, chemical, thermal or supercritical extraction, and further fermented using fungi or yeast such as *Saccharomyces cerevisiae*, *Kluyveromyces fragilis*, *Torulaspora* and *Zymomonas mobilis* (Chen *et al.*, 2013). Ethanol concentrations of 12-15 gL^{-1} can be achieved when processing microalgae concentrations of 50 g L^{-1}.

Finally, it should be highlighted that the high costs of microalgae production, which directly impacts on the cost of biofuels, can be mitigated by using residual CO_2 sources (such as industrial emissions) and wastewaters.

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