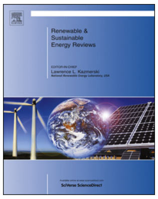
Renewable and Sustainable Energy Reviews 44 (2015) 20–36

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



Algae as promising feedstocks for fermentative biohydrogen production according to a biorefinery approach: A comprehensive review

Cecilia Sambusiti [a,*], Micol Bellucci [a], Anastasia Zabaniotou [a,b],
Luciano Beneduce [a], Florian Monlau [a]

[a] *STAR Agroenergy Research Group, University of Foggia, Via Gramsci, 89-91, 71121 Foggia, Italy*
[b] *Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece*

ARTICLE INFO

Article history:
Received 14 August 2014
Received in revised form
18 November 2014
Accepted 12 December 2014

Keywords:
Biohydrogen
Biorefinery
Dark fermentation
Macroalgae
Microalgae
Pretreatment

ABSTRACT

Interest is growing in the production of biohydrogen from algae through dark fermentation, as alternative to fossil fuels. However, one of the limiting steps of biohydrogen production is the conversion of polymeric carbohydrates into monomeric sugars. Thus, physical, chemical and biological pretreatments are usually employed in order to facilitate carbohydrates de-polymerization and enhancing biohydrogen production from algae. Considering the overall process, biohydrogen production through dark fermentation leads generally to negative net energy balances of the difference between the energy produced as biohydrogen and the direct ones (heat and electricity) consumed to produce it. Thus, to make the overall process economically feasible, dark fermentation of algae must be integrated in a biorefinery approach, where the outlets are valorized into bioenergy or value added biomolecules.The present study reviews recent findings on pretreatments and biohydrogen production through dark fermentation of algae looking at the perspectives of integrating side streams of dark fermentation from algal biomass, according to a biorefinery approach.

Contents

Abbreviations: AD, anaerobic digestion; BHP, biological hydrogen potential; BBD, Box–Behnken design; BESA, 2-bromoethanesulfonic acid; COD, chemical oxygen demand; DF, dark fermentation; ECE, energy conversion efficiency; FHP, fermentative hydrogen potential; HMF, hydroxylmethylfurfural; HPB, hydrogen producing bacteria; HRT, hydraulic retention time; LHW, liquid hot water; MEC, microbial electrolysis cells; MFC, microbial fuel cell; MOW, mariculture organic waste; OLR, organic loading rate; PHA, polyhydroxyalkanoates; PF, photofermentation; RSM, response surface methodology; S/L, solid to liquid ratio; TS, total solids; VFA, volatile fatty acids; VS, volatile solids

[*] Corresponding author. Present address: INRA, UMR 1208, IATE Ingenierie des Agropolymères et Technologies Emergentes, 2, Place Pierre Viala – Bât 31, 34060 Montpellier cedex 1, F-34060, France. Tel.: +33 4 99 61 25 81; fax: +33 4 99 61 30 76.

E-mail addresses: cecilia.sambusiti@supagro.inra.fr, cecilia.sambusiti@gmail.com (C. Sambusiti), micol.bellucci@gmail.com (M. Bellucci), azampani@auth.gr (A. Zabaniotou), luciano.beneduce@unifg.it (L. Beneduce), flomonlau@hotmail.fr (F. Monlau).

http://dx.doi.org/10.1016/j.rser.2014.12.013
1364-0321/

1. Introduction

Depletion of fuels, environmental pollution and climate change compels the search for sustainable and environmental sources of energy to sustain the industrial economy and society [1]. In this context, macro and micro-algae offers a huge potential for the production of biofuels. If used in a sustainable way, algal biomass could be beneficial for the reduction of the world's dependency on oils, as well as the global emission of greenhouse gases [2]. Solid (pellets, wood chips), liquid (bioethanol, vegetable oil and biodiesel) or gaseous (biogas, biohydrogen) biofuels can be categorized into 1st, 2nd and 3rd generations according to the origin of the biomasses used [3].

Recently, the use of first generation biofuels from agricultural substrates, traditionally destined for food and animal purposes, raised controversial debates due to the “food versus fuel” dilemma [4,5]. This led to the development of 2nd generation biofuels (bioethanol, biohydrogen, methane) produced from non-food biomass, such as crop residues (corn stover, manure, straw, waste wood) and energy crops cultivated on no arable lands (miscanthus, sorghum, poplar, willow, switchgrass) [6–8]. The use of these lignocellulosic substrates presents several advantages, since they are abundant renewable non-food materials and do not create competition for lands with food crops. Nevertheless, contrarily to first generation biofuels, the production of second generation fuels is still not cost effective. Indeed, expensive pretreatment steps are required to defeat the intrinsic compositional and physical barriers of lignocellulosic matrices in order to convert such substrates into biofuels [9,10].

In this light, 3rd generation biofuels derived from algae could be considered as another viable alternative energy source that is devoid of the major drawbacks associated with the first and second-generation biofuels [3,11–13]. Indeed, algae present several advantages compared to terrestrial plants: (i) higher growth rate with superior CO_2 fixation capacity; (ii) they do not need arable land to grow; (iii) they do not contain lignin. Nevertheless, the cultivation of microalgae requires high water use and high initial investment that can make the process still not economically appealing [14].

Biohydrogen production trough dark fermentation (DF) process has gained increased attention in last years, mainly due to process simplicity and possibility to convert a wide range of substrates [7]. Moreover, hydrogen gas presents a high-energy yield (122 kJ g^{-1}); its combustion generated only water vapour and its surplus can be stored and used when needed [15]. Like starch- and lignocellulosic-based substrates, algal biomass as a feedstock for DF biohydrogen production requires firstly the conversion of polymeric carbohydrates into readily accessible monomeric sugars [16]. Anaerobic mixed cultures are characterized by low hydrolytic enzymatic activity; consequently a pre-treatment step is often required to enhance the hydrolysis of algae biomass [7,17]. So far, among the different pretreatment categories (physical, chemical and biological), the most commonly used to enhance carbohydrates hydrolysis of micro and macroalgae are physical (milling, ultrasonic, microwave), thermal (LHW, steam explosion,) and thermo-chemical pretreatments. However, the major drawback of using thermal and thermo-chemical pretreatments is the possible formation of by-products, such as aliphatic acids and furan derivatives (furfurals and 5-HMF), which can inhibit the action of enzymes and/or further reduce the sugar conversion into H_2 [18,19].

Finally, biohydrogen production through dark fermentation leads generally to negative net energy balances as of the difference between the energy produced and the direct ones (heat and electricity) consumed to produce it [15]. Furthermore, during carbohydrates conversion, only 1/3 is directed to H_2 producing pathways and most of the hydrogen equivalents are still incorporated in Volatile Fatty Acids (VFAs) (i.e. butyrate, acetate) or solvents (i.e. ethanol, acetone) [20]. Acid metabolites accumulation in DF process can also cause a sharp drop of pH, resulting in the failure of the process [21]. Consequently, to be sustainable, dark fermentation must be integrated in a biorefinery approach where the outlets are valorised for bioenergy production or valuable added compounds (Fig. 1). For this purpose, the solid phase could be partially converted into methane through anaerobic digestion process or into other biofuels using thermo-chemical conversion processes (i.e. co-gasification, co-pyrolysis) [22,23]. Recently, the valorization of liquid effluents which are rich in VFAs (mainly acetate and butyrate) has attracted a lot of attention [24,25]. Among them, biogas production through anaerobic digestion [26], photofermentation [27,28] and bio-electrochemical systems such as microbial fuel cells (MFC) or microbial electrolysis (ME) [21,29] as well as heterotrophic microalgae cultivation [30] and value added molecules (PHAs) [31] have been reported.

The objective of the present study is to review recent findings on biohydrogen production from algae through dark fermentation. For this purpose, the following points are discussed: (a) chemical characterization of macro and microalgae; (b) screening of biohydrogen potentials of different algal species and limiting factors that influence their efficient conversion into biohydrogen; (c) effect of pretreatments to enhance biohydrogen production from algae; (d) investigation of various valorisation routes of dark fermentation outlets of algae according to a biorefinery approach.

2. Algae biomass

Microalgae and macroalgae are simple chlorophyll containing organisms which are able to photosynthetically convert atmospheric carbon dioxide into a wide range of metabolites and chemicals including proteins, hydrogen, polysaccharides and/or lipids [32].

For these reasons, they have received great attention as novel biomasses to produce biofuels (i.e. biodiesel, bioethanol, biogas,