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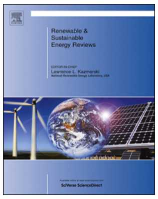

Fermentative hydrogen production using algal biomass as feedstock

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ABSTRACT

Hydrogen is considered as an ideal alternative to fossil fuels due to its high energy density by mass and clean combustion product. Using anaerobic bacteria to ferment biomass and produce renewable hydrogen is receiving increased attention. Aquatic algal biomass, which can be sourced from natural algal bloom or mass cultivation, is considered as a promising substrate for hydrogen fermentation. This paper reviews the recent developments in fermentative hydrogen production from algal biomass, with the main focus on hydrogen production potential and its current technological state. The stoichiometric hydrogen yields of algal biomass in dark fermentation are predicted based on the theoretical contents of monosaccharides from carbohydrates and glycerol from lipids in biomass. Hydrogen yields of algal biomass by dark fermentation can be improved by using efficient pretreatments at optimized biomass carbon/nitrogen ratios with domesticated hydrogen-producing bacteria as the inoculum. The effluent of dark fermentation, which is rich in volatile fatty acids, should be used for the production of biofuels and biochemicals to further improve the energy efficiency and economic feasibility of hydrogen fermentation.

Contents

Abbreviations: AF, anaerobic filter; ATP, adenosine triphosphate; COD, chemical oxygen demand; CSTR, continuous stirred tank reactor; DHAP, dihydroxyacetone phosphate; DW, dry weight; HPB, hydrogen-producing bacteria; HRT, hydraulic retention time; LCFA, long-chain fatty acid; MPB, methane-producing bacteria; NADH, reduced nicotinamide adenine dinucleotide; PKP, phosphoketolase pathway; PPP, pentose phosphate pathway; TAG, triacylglycerol; UASB, up-flow anaerobic sludge bed; VFA, volatile fatty acid; VS, volatile solids.

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1. Introduction

The extensive utilization of non-renewable fossil fuels has led to serious energy crisis and environmental problems [1–3]. Hydrogen is considered as an ideal alternative to fossil fuels because of its high energy density by mass (higher heating value: 142 kJ/g) and clean combustion product (H_2O) [4–6]. Hydrogen can be produced from many conventional processes, such as water electrolysis and steam reforming. Nevertheless, these processes are highly energy intensive and not environmentally friendly [4,7,8]. Renewable hydrogen production from biomass by hydrogen-producing bacteria (HPB) by biological anaerobic dark fermentation is receiving increased attention because of its energy saving, environmentally friendly, and carbon-neutral characteristics [9–13].

The choice of biomass feedstock is a crucial issue in biofuel production [14]. Biofuels may be derived from land-based crops, such as maize and sugarcane. The technologies for cultivation, harvesting, and biofuel conversion of land-based crops are mature. However, biofuels derived from land-based crops have drawn criticisms, due to the competition of food production and large consumption of fresh water and fertilizer [15,16]. In contrast, aquatic algae, which can be classified as either microalgae (e.g., *Chlorella*, *Chlamydomonas*, and *Arthrospira*) or macroalgae (e.g., *Laminaria*, *Ulva*, and *Gelidium*) based on their morphology and size [17–22], may offer promising options for the biofuel production because of the following reasons. Firstly, biofuel yields from algae in same cultivation area are 10–100 times higher than those from land-based crops because of their short biomass doubling time (as short as 3.5 h) and high productivities [up to 26,300 t dry weight (DW)/km^2/yr] [11,18,23–28]. Secondly, algae do not need arable land for mass cultivation because they are aquatic species [19,29,30]. Thirdly, algal biomass contains little or no lignin, which enables easy hydrolysis of the biomass for subsequent hydrogen fermentation [17,20]. Hydrogen production by dark fermentation using algae as substrates has attracted considerable attention in recent years [10,31–37]. However, comprehensive review on this issue is limited. Furthermore, to our knowledge, the stoichiometric hydrogen production potential of complex biomass, such as algal biomass, has not been reported in the literature.

Less than 1/3 of energy in glucose can be converted to hydrogen in dark fermentation, whereas more than 2/3 of energy remains in the dark fermentation effluent in the forms of soluble metabolite products (SMPs), including volatile fatty acids (VFAs; e.g., acetate and butyrate) and alcohols (e.g., ethanol) [38]. Further conversion of the SMPs to biofuels and biochemicals can significantly improve the energy efficiency and economic feasibility of hydrogen fermentation [39].

This paper focuses on the discussion of hydrogen production based on the monomers derived from biomass, with a particular attention for algal biomass. The theoretical hydrogen potential of algal biomass is comprehensively discussed, and the current state of hydrogen fermentation technology is evaluated. Furthermore, the challenges associated with algal hydrogen fermentation are highlighted. The detailed objectives of this paper are to (1) analyze the metabolic pathways and theoretical yields of hydrogen production from the monomers of organic components (e.g., carbohydrates, proteins, and lipids) derived from algal biomass during dark fermentation, (2) discuss the effects of pretreatments on hydrogen production from algal biomass during dark fermentation, (3) compare the hydrogen production via dark fermentation and methane production via anaerobic digestion using algae as substrates, (4) discuss the further conversion of SMPs to biofuels and biochemicals, (5) propose an efficient process to convert algal biomass to hydrogen, and (6) estimate the potential of algal hydrogen fermentation in China.

2. Stoichiometric potential of dark hydrogen production from algal biomass

In dark fermentation, high-molecular weight organic substrates (e.g., carbohydrates, proteins, and lipids) are first hydrolyzed to low-molecular weight ones (e.g., monosaccharides, amino acids, and glycerol), and then are converted to SMPs, hydrogen, and carbon dioxide by HPB [40]. Hydrogenase is the key enzyme that catalyzes molecular hydrogen formation by combining protons and electrons [9]. Typical bacteria genera that are related with dark fermentation are *Clostridium*, *Enterobacter*, *Lactobacillus*, *Bacillus*, *Klebsiella*, *Citrobacter*, *Anaerobiospirillum*, *Thermotoga*, and *Caldicellulosiruptor* [41,42]. Dark fermentation is mainly composed of hydrolysis and acidogenesis of anaerobic digestion [43]. However, given that slow hydrolysis conducted by HPB seriously constrains subsequent acidogenesis for hydrogen production, additional pretreatment for biomass with high-molecular weight components is necessary [11,44].

2.1. Metabolism of carbohydrates in dark fermentation

High-molecular weight carbohydrates should generally be hydrolyzed to monosaccharides, which can then be efficiently used by HPB during dark fermentation [45]. Glucose, which is the most abundant and typical hexose, can be stored in the forms of starch, glycogen, cellulose, and trehalose in algal biomass [10,20,46–48]. A number of studies have reported the metabolic pathways of glucose during dark fermentation (Fig. 1) [46,49–51]. Glucose is degraded by HPB into pyruvate, coupled with generation of reduced nicotinamide adenine dinucleotide (NADH). Pyruvate is degraded into lactate (end product) by consuming NADH, or converted into acetyl-CoA, coupled with (1) generation of NADH and carbon dioxide, or (2) generation of hydrogen and carbon dioxide, or (3) generation of formate. Formate is further degraded into hydrogen and carbon dioxide as shown in Eq. (1) [52]. Acetyl-CoA is further converted into end products, such as ethanol, butyrate, and acetate, with or without consuming NADH. NADH and H^+ generate hydrogen by catalysis of HPB hydrogenase (1 mol NADH generates 1 mol hydrogen) as shown in Eq. (2) [4]. The NADH generation and consumption during glucose metabolism are shown in Table 1. 1 mol glucose can theoretically generate 4 mol NADH through the acetate pathway. Therefore, 1 mol