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Fermentative hydrogen production using lignocellulose biomass: An overview of pre-treatment methods, inhibitor effects and detoxification experiences

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ABSTRACT

Biohydrogen production from lignocellulosic biomass (LCB) is an active research area. Several workers have tested a number of substrates under different operational conditions and brought forward the many positive process performance features and identified the main sources of inhibition. This review analyzes selected fermentative biohydrogen production processes by revisiting the core biohydrogen production performances in terms of gas production rates and yields and equally addresses the options for process enhancement by the application of through pretreatment methods and detoxification of process inhibitors. In addition, the issues related to continuous biohydrogen operation in different reactor configurations are highlighted. Lastly, future avenues of research which may be engendered and engineered to enhance the biohydrogen generation and process biokinetics are discussed. This review intends to provide the fundamental understanding of biohydrogen production and provides a perspective on future developments in this area of applied research.

1. Introduction

Every day human life is dependent on various forms of energy. Nowadays, the energy-related science and engineering have paid remarkable attention to hydrogen gas (H_2), as a prospective fuel candidate. The unique characteristics of H_2 such as its high gravimetric-based energy content, absence of greenhouse gas emissions after its combustion/oxidation and its relatively versatile production methods have qualified it to the potential contributors of future energy demand. Hence, the exploitation of alternative energy carriers such as hydrogen could facilitate environmental-friendly, cleaner technologies and consequently, it would lead to higher sustainability and the wiser use of limitedly available fossil resources [1].

The H_2 formation via biotechnological methods is considered to be an important process in achieving the transition and development of a green energy market. First reports on hydrogen production by fermentative pathways date back to the early 1970's [2]. Thereafter, the magnitude of research efforts dealing with various aspects of hydrogen fermentation, including feedstock utilization, reactor design and engineering, insights to microbial community structures, metabolic engineering or modification of hydrogenases, post-fermentation downstream (i.e. H_2 purification and upgrading) has been growing tremendously. Especially in these last 5 years, it has grown enormously (Fig. 1). Although fermentative hydrogen production could have

Abbreviations: LCB, Lignocellulosic biomass; H_2, Hydrogen gas; US, United States of America; ATP, Adenosine triphosphate; H^+, Protons; SHF, Separate hydrolysis and fermentation; SSF, Simultaneous saccharification and fermentation; C_5, Pentose sugars; C_6, Hexose sugars; 5-HMF, 5-hydroxy methyl furfural; PCR-DGGE, Polymerase chain reaction-denaturing gradient gel electrophoresis; CE-SSCP, Capillary electrophoresis-single strand conformation polymorphism; CSTR, Continuous stirred tank reactor; SBR, Sequencing batch reactor; HRT, Hydraulic retention time; OLR, Organic loading rate; UHB, Unhydrolysed biomass; DJW, De-oiled jatropha waste; HHV, High heat value; AC, Activated carbon; CH_4, Methane gas; h, Hour; PHAs, Polyhydroxyalkanoates

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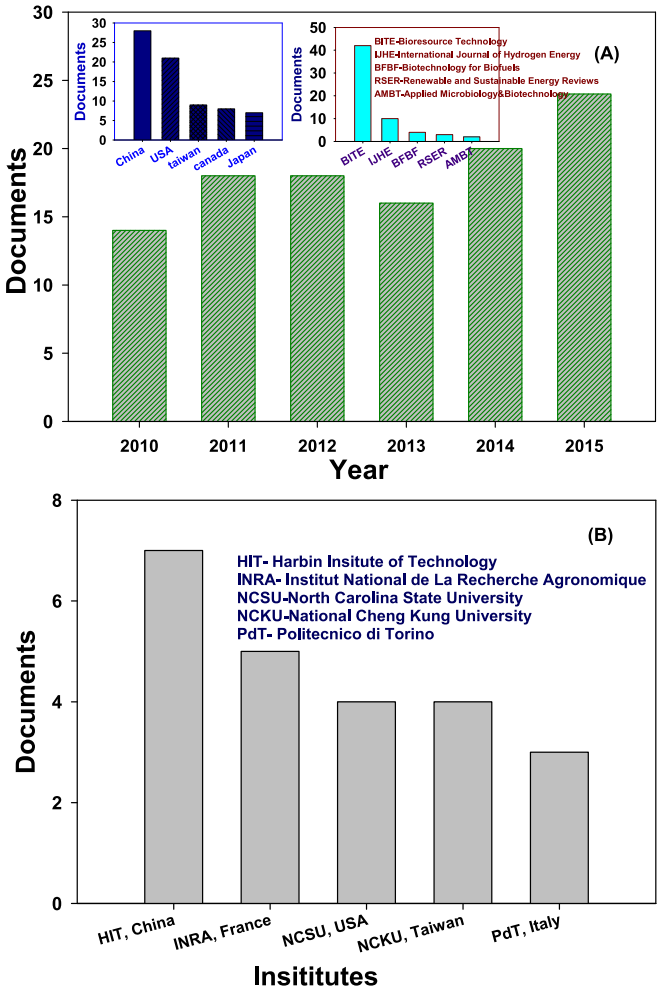

Fig. 1. Literature survey of LCB to H_2 (in the last five years).

compromises due to appearance of side-products such as volatile fatty acids, their conversion has been demonstrated by several promising approaches [3]. Although, from a technological point of view, continuously operated bioreactors are the most suggestible for up-scaled future implementations (a dominant part of previous works on continuous fermentative hydrogen production was carried out using glucose and sucrose). However, comparatively, only a fewer number of studies have been presented based on sugar-rich wastewater streams [4] and maybe even less based on complex structure solid materials, in particular lignocelluloses [1]. Nevertheless, the further expansion of these research directions would be essential for industrially and economically viable applications.

Glycerol, as a major byproduct (about 10%) of biodiesel production which has been widely used as substrate in anaerobic digestion due to its easily degradable property. Glycerol has also been found to be a relatively cheap and effective substrate for the generation of hydrogen under fermentative processes. Ito et al. [5] have worked on the generation of hydrogen from manufacturing wastes which contained glycerol using *Enterobacter aerogenes* HU-101. They reported that the yields of hydrogen had increased with the concentrations of glycerol and that the rates of hydrogen generation were significantly higher with the pure glycerol at the same concentration in comparison with other substrates they had analyzed in their work. Ito et al. [5] calculated a peak rate of hydrogen generation of 80 mmol/L/h from pure glycerol. Selembo et al. [6] reported that the fermentation of glycerol had resulted in the generation of 0.28 mol hydrogen/mol-glycerol. Seifert et al. [7] studied the effect of glycerol concentration on the hydrogen production under dark fermentative conditions in batch experiments. Seifert et al. [7] reported that the maximum hydrogen yield had reached 0.41 mol hydrogen for every mole of glycerol and this performance had been possible with 10 g/L of glycerol in aqueous medium. Seifert et al. [7] also reported that higher concentrations of glycerol of up to 30 g/L had produced more effective hydrogen production reaching 0.7 L H_2/L of medium. Sabourin-Provost and Hallenbeck [8] demonstrated that *Rhodopseudomonas palustris* is able to convert pure and crude glycerol into hydrogen using photo-fermentation, and reported high yields of reaching as high as 6 mol hydrogen for every mole of glycerol. One interesting result from this work of Sabourin-Provost and Hallenbeck [8] was that crude glycerol had readily produced hydrogen with no constraint of toxicity and inhibition. Maru et al. [9] have reported the fermentation of glycerol using *T. maritima* in batch chemostat units obtained a peak yield in the tune of 0.8 mol hydrogen/ mol glycerol. Maru et al. [10] have later further investigated the potential of producing biohydrogen from glycerol using *Enterobacter* spH1, *Enterobacter* spH2, and *Citrobacter freundii* H3 and found that with a starting concentration of 20 g/L for the glycerol substrate, all the bacterial strains had yielded very high amounts of hydrogen in the range of 2400–3500 mL/L. Liu et al. [11] proved that glycerol purification does not necessarily improve the production dynamics of hydrogen during anaerobic fermentative processes. Pachapur et al. [12] have recently studied the co-fermentation of crude glycerol with apple pomace hydrolysate, and reported that with the hydrolysate, the oxidative mechanistic route had been favored to give a higher hydrogen generation at 26.07 mmol/L and a lowering in the levels of by-products formation. A continuous production of biohydrogen from crude glycerol using an anaerobic up-flow column bioreactor (UFCB) has been reported earlier [13]. In the latter study, the maximum biohydrogen generation was 107.3 ± 0.7 L/kg waste glycerol under optimal conditions was reported [13]. Fountoulakis et al. [14] reported that supplementation of crude glycerol with olive mill wastewater and slaughterhouse wastewater increases methane and hydrogen production. Hydrogen yield was increased from 15 mmol H_2/g VS to 26 mmol H_2/g VS added after the addition of glycerol. Recently Zahedi et al. [15] demonstrated that almost doubled hydrogen production and specific hydrogen production rates were achieved after addition of 1% v/v crude glycerol to the industrial municipal solid waste under dark fermentation in batch mode. Sharma et al. [16] reported the bioenergy production in the form of hydrogen and electricity from pure glycerol and glycerol derived from biodiesel waste streams using microbial fuel cells (MFCs) and hydrogen producing bioreactors (HPBs). The maximum hydrogen production 0.20 mol H_2/mol glycerol and 0.17–0.18 mol H_2/mol glycerol from pure glycerol and glycerol from biodiesel waste stream, respectively.

Trchounian et al. [17] have demonstrated that *Escherichia coli* wild type BW25113 has occasioned significantly improved biohydrogen generation yields from glycerol (up to 0.77 mmol/L) when the biosynthesis was assisted by combinations of the following micronutrients: Ni^{2+}, Fe^{3+} and Mo^{6+}. Maru et al. [18] reported that a mixed culture of *Enterobacter* spH1 and *E. coli* CECT432 has produced a 3.1-fold more pronounced yield of biohydrogen when crude glycerol has been fermented under dark conditions. Cofré et al. [19] have studied recently the bioconversion of crude glycerol into biohydrogen by *Escherichia coli* MG1655 and reported having achieved almost complete consumption of the glycerol to reach a final biohydrogen yield of 0.56 mol/mol crude glycerol fed to the system. Very recently, Valle et al. [20] have developed a unique metabolic engineering approach and demonstrated a considerable enhancement in the production of biohydrogen from glycerol using *E. coli* which had been accompanied by the redirection of C4 metabolites. Soo et al. [21] have also used a genetically engineered type of recombinant *E. coli* (having "*hycE and recombinant E. coli with hydA*") and demonstrated that there had been a significantly larger biohydrogen yield of up to 20% when glycerol has been metabolized.