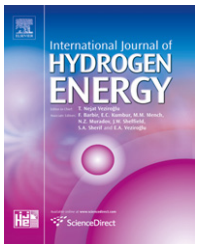
Available at www.sciencedirect.com

ScienceDirect

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



Influence of pH on fermentative hydrogen production from sweet sorghum extract

Georgia Antonopoulou [a,b,*], *Hariklia N. Gavala* [a,b,1], *Ioannis V. Skiadas* [a,b,1], *Gerasimos Lyberatos* [a,b]

[a] *Department of Chemical Engineering, University of Patras, 1 Karatheodori st., GR 26500 Patras, Greece*
[b] *Institute of Chemical Engineering and High Temperature Chemical Processes, GR 26504 Patras, Greece*

ARTICLE INFO

Article history:
Received 14 July 2009
Received in revised form
28 December 2009
Accepted 28 December 2009
Available online 13 January 2010

Keywords:
Sweet sorghum
Hydrogen
pH
Continuous fermentation
Biohydrogen

ABSTRACT

The present study focused on the influence of pH on the fermentative hydrogen production from the sugars of sweet sorghum extract, in a continuous stirred tank bioreactor. The reactor was operated at a Hydraulic Retention Time of 12 h and a pH range of 3.5–6.5. The maximum hydrogen production rate and yield were obtained at pH 5.3 and were 1752 ± 54 mL H_2/d or 3.50 ± 0.07 L H_2/L reactor/d and 0.93 ± 0.03 mol H_2/mol glucose consumed or 10.51 L H_2/kg sweet sorghum, respectively. The main metabolic product at this pH value was butyric acid. The hydrogen productivity and yield were still at high levels for the pH range of 5.3–4.7, suggesting a pH value of 4.7 as optimum for hydrogen production from an economical point of view, since the energy demand for chemicals is lower at this pH. At this pH range, the dominant fermentation product was butyric acid but when the pH culture sharply decreased to 3.5, hydrogen evolution ceased and the dominant metabolic products were lactic acid and ethanol.

1. Introduction

Global climate change due to the increased carbon dioxide emissions along with concerns over depletion of the fossil fuel resources have aroused increased interest in alternative energy strategies [1]. In this respect, hydrogen has become one of the most attractive energy carriers, because it is clean, has a high-energy yield (122 kJ/g) and its production via biological means has the potential to eliminate environmental deterioration due to the utilization of conventional fossil fuels [2]. Biological hydrogen may be produced by cyanobacteria and algae through biophotolysis of water or by photosynthetic and chemosynthetic-fermentative bacteria [3]. The fermentative hydrogen production process has the advantages of high hydrogen efficiency, simplicity of control, low production cost and light – independence compared to the photosynthetic process [4,5]. Moreover, a variety of renewable biomasses such as wastes and energy crops can be used as feedstock, while metabolites of commercial interest, such as organic acids and solvents, are also generated [6].

Fermentative hydrogen production is carried out under anoxic conditions. When organic substrates are degraded by fermentative bacteria, electrons which need to be disposed of to maintain electrical neutrality are produced, while protons act as electron acceptors and molecular hydrogen is produced [7]. When glucose is used as the model substrate for

* Corresponding author. Department of Chemical Engineering, University of Patras, 1 Karatheodori st., GR 26500 Patras, Greece. Tel.: +30 2610969577; fax: +30 2610993070.
E-mail address: geogant@chemeng.upatras.gr (G. Antonopoulou).
[1] Present address: Department of Biotechnology, Chemistry and Environmental Engineering, Copenhagen Institute of Technology (Aalborg University Copenhagen), Lautrupvang15, DK 2750, Ballerup, Denmark.
0360-3199/$ – see front matter © 2010 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2009.12.175

fermentative hydrogen production, it is first converted by hydrogen-producing bacteria via the glycolytic pathway, to pyruvate which can be further converted to a number of soluble metabolites, i.e. acetic, propionic, butyric and lactic acids, ethanol etc. Hydrogen is produced either from the reduced form of ferredoxin or through the decomposition of formic acid when acetyl-CoA is produced from pyruvic acid (reactions (1) and (2)).

$$\text{Pyruvate} + \text{CoA} + 2\text{Fd(ox)} \rightarrow \text{acetyl-CoA} + CO_2 + 2\text{Fd (red)} \quad (1)$$

$$\text{Pyruvate} + \text{CoA} \rightarrow \text{acetyl-CoA} + \text{formic acid} \quad (2)$$

Production of acetic and butyric acids favours production of hydrogen, with the fermentation to acetic acid giving the highest theoretical yield of 4 mol H_2/mol glucose, while the conversion of glucose to butyric acid yields 2 mol H_2/mol glucose [8,9]. The production of other, more reduced organic acids and/or alcohols lowers the yield of H_2, namely glucose conversion to propionic acid and ethanol leads to negative and zero yield of hydrogen, respectively [10].

In mixed acid fermentation processes, the involved microorganisms produce rather a spectrum of metabolic products than only acetic acid, which consequently leads to lower than the maximum theoretical hydrogen yields. Selection of pathway and consequently, hydrogen and fermentation end-products distribution, is highly dependent on many factors, such as wastewater specificity, reactor configuration, Hydraulic Retention Time (HRT), influent organic concentration, organic loading rate, pH, temperature, oxidation-reduction potential, nutritional requirements, the absence or deliberate inhibition of hydrogenotrophic methanogens etc. [11–15]. Among these factors, pH, which strongly influences hydrogenase activity [16] and metabolic pathways selection [17] is especially important. In addition, pH variation can also affect cell morphology and structure and thus flocculation and adhesion phenomena [18]. If pH is not maintained in the optimal range, it may inhibit hydrogen production or even cause a microbial population shift resulting in cessation of hydrogen production [19]. Therefore, the control of pH is crucial.

Up to now, the effect of pH on hydrogen production by mixed microbial cultures using synthetic substrates such as glucose [20–22], sucrose [23,24] and starch [25], has been investigated. However, there is a wide range of pH values, which have been proposed as optimum for fermentative hydrogen production from different feedstocks. The pH range of 5–7.5 [20,26] is usually reported as optimum, even though lower or higher pH values such as pH of 4.5 [27] and 9.0 [28] have also been proposed to give the maximum hydrogen yield. This could be attributed to the differences among these studies in terms of inocula, operation mode and the pH range studied.

Up to now the majority of studies report the influence of initial pH on fermentative hydrogen production at batch systems [12,29,30]. Although batch mode fermentative hydrogen production is frequently carried out for research purposes [21,28] industrially feasible processes would most likely have to be performed on a continuous or at least semi-continuous (fed or sequencing batch) basis. So far, little information is available in the relevant literature concerning the role of pH in continuous fermentative hydrogen production process [20,25].

In the present study the effect of pH on the continuous hydrogen production from sweet sorghum extract, was investigated. Sweet sorghum is an annual plant of tropical origin, well-adapted to sub-tropical and temperate regions, highly productive in biomass and rich in readily fermentable sugars [10,31]. Recently, we demonstrated the feasibility of fermentative hydrogen production from sweet sorghum extract at different HRTs [10]. We reported that at the HRT of 12 h and a pH value of 5.3, maximum hydrogen yield was obtained using as inoculum the indigenous mixed microbial culture already contained in the sweet sorghum extract. In the present study, the influence of pH on the hydrogen production rate and yield was investigated and the possibility of high hydrogen yields at low pH values was explored with the additional advantage of decreased addition of chemicals. In general, the operation of a fermentative hydrogen production reactor at low pH values has the advantage of reduced consumption of chemicals in order to maintain the pH at levels allowing for hydrogen production. Thus, the contribution of the operational cost to the total cost of the process will be lower compared to the case of the reactor operation at higher pH value. So, hydrogen production at low pH values results in an improvement of the process efficiency from an economic point of view.

2. Materials and methods

2.1. *Analytical methods*

Determinations of chemical oxygen demand of the mixed liquor (TCOD) or of only the soluble part (SCOD), total suspended solids (TSS) and volatile suspended solids (VSS) were carried out according to Standard Methods [32]. For the quantification of volatile fatty acids (VFA) and ethanol (EtOH), 1 mL of filtered sample acidified with 30 μL of 20% H_2SO_4 was analyzed on a gas chromatograph (VARIAN CP-30), equipped with a flame ionization detector and a capillary column (Agilent technologies, INC. 30 m × 0.53 mm). The oven was programmed from 105 °C to 160 °C at a rate of 15 °C/min, and subsequently to 235 °C (held for 3 min) at a rate of 20 °C/min for VFA analysis and from 60 °C (held for 1 min) to 230 °C (held for 0.5 min) at a rate of 45 °C/min for ethanol analysis. Helium was used as the carrier gas at 15 mL/min, the injector temperature was set at 175 °C and the detector at 225 °C and 200 °C, for VFA and ethanol determinations respectively. The concentration of lactic acid was measured on a liquid chromatograph (DIONEX DX300), equipped with an electron conductivity detector and a Dionex IonPac column (AS11-HC, 4 × 250 mm Analytical). The eluent (sodium hydroxide solution) flow rate was 1.5 mL/min and the analysis was carried out at 30 °C. The produced gas composition in hydrogen and methane was quantified with a gas chromatograph (VARIAN STAR 3600) equipped with a thermal conductivity detector and a packed column with nitrogen as carrier gas. The injector, column and detector temperatures were set at 70 °C, 80 °C and