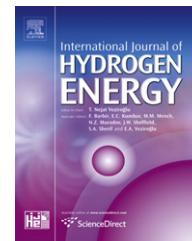


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Continuous production of hydrogen from oat straw hydrolysate in a biotrickling filter

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ABSTRACT

Hydrogen was produced in a biotrickling filter (BF) packed with perlite and fed with oat straw acid hydrolysate at 30 °C. Inlet chemical oxygen demand (COD) from 1.2 to 35 g/L and hydraulic retention time (HRT) between 24 h and 6 h were assayed. With increasing inlet COD or decreasing HRT, H₂ production rate (HPR) increased but H₂ production yield (HY) decreased. Maximum HPR of 81.4 mL H₂/L_{reactor} h (3.3 mmol H₂/L_{reactor} h) and HY of 2.9 mol H₂/mol_{hexose consumed} were found at an inlet COD of 0.05 g_{COD}/L h (HRT 24 h) and 2.9 g_{COD}/L h (HRT 12 h), respectively. Maximum hydrogen composition in gas was 45 ± 4% (v/v) with CO₂ as balance. Methane was not detected. Maximum HPR and inlet COD used in this work were higher than others reported for reactors with suspended or fixed biomass. However, implementation of strategies for biomass control to avoid reactor clogging is needed.

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1. Introduction

Currently, hydrogen is considered an alternative to fossil fuels. It may be favored over methane because hydrogen is not chemically bound to carbon, and therefore, when burned it does not contribute to greenhouse gases or acid rain [1]. Also, hydrogen has a high energy yield of 122 kJ/g, which is 2.75 times greater than hydrocarbon fuels [2]. However, hydrogen is currently produced mainly from natural gas, a non-renewable resource, through steam reforming, a process that generates large quantities of carbon dioxide (CO₂), one of the main causes of global warming.

Many investigations have been conducted using model substrates (i.e. glucose and sucrose) and pure cultures of hydrogen-producing bacteria [3–5]. Also, biohydrogen production is usually conducted via continuous flow stirred tank reactors [6–8] because these are easy to operate and can provide a good substrate-biomass contact by vigorous mixing. However, one of the major limitations of continuous stirred

tank bioreactors (CSTR) is their low cell retention, especially when operating at a high dilution rate (i.e. low hydraulic retention time, HRT), resulting in low H₂ production efficiency due to cell washout [9]. To cope with this problem, there is a need to develop H₂ production systems able to retain sufficient active H₂ producing biomass in the reactor while operating at high organic loading rate and short hydraulic retention times. One strategy among several to retain biomass that has been reported in the literature is the use of membrane bioreactors in which high cell retention can be attained. However the operation of these reactors has been limited to lab studies due to high costs, caking and fouling problems [10]. Another strategy is the use of packed bed or trickling reactors in order to enhance H₂ production [11–19]. In all these studies simple substrates like sucrose or glucose were used for hydrogen production. Reported values of H₂ production rates (HPR) and H₂ yields (HY) in packed bioreactors using simple substrates were in the range between 311 and 8.9 mmol H₂/L h and 2.8 to 0.54 mol H₂/mol_{hexose},

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respectively. Also, various studies have been carried out using complex biodegradable substrates like starch [6,20–22] or starch hydrolysate [23] for hydrogen production.

Microbial production of hydrogen (biohydrogen) from renewable organic waste sources, such as agricultural wastes, represents an important area of biofuel production because one of the main challenges is to produce H_2 at commercial scale from low cost feedstock to achieve sufficient and cost-effective energy supplies. Consequently, the substrate used for fermentative H_2 production must be abundant, easily available, and inexpensive. Agricultural wastes meet these requirements and could be a commercially feasible biohydrogen feedstock [23]. However, the direct use of agricultural wastes as substrates for microbial hydrogen production is hindered by the low biodegradability of the lignocellulosic matrix present in the straw wastes. To handle this limitation, various agricultural waste pretreatments have been reported with the objective to release the easily biodegradable fractions contained in these wastes (i.e. hydrolysates containing hexoses and pentoses) and thus, obtaining a more suitable substrate to produce biohydrogen [23–26]. Several reports have been published on the microbial production of hydrogen using lignocellulosic substrates such as sugarcane bagasse hydrolysates [26], wheat straw hydrolysate [27,28], cornstalk and corn stover hydrolysates [29–32], and cellulosic hydrolysate [33]. All of these studies were conducted in batch mode or in continuous systems [27,28]. To the best of our knowledge, there is only one recent report in the literature on the use of a thermophilic anaerobic filter for H_2 production from lignocellulosic hydrolysates [32]. Thus, the present study was conducted with the aim to further investigate the use of a mesophilic bio-trickling filter (BF) to achieve high microbial densities for the production of hydrogen by using oat straw acid hydrolysates. Different HRT and inlet organic concentrations were assayed to evaluate the performance of the BF reactor and to found the maximum production rate of hydrogen.

2. Materials and methods

2.1. Inoculum

A mixture of two anaerobic granular sludges, both treating industrial wastewater, was used to inoculate the reactor; one sludge sample was obtained from an UASB reactor located at a malt industry (Central de Malta S.A. Puebla, México). This sludge was previously acclimatized in our laboratory to produce hydrogen from straw wastes. The other sludge was obtained from an UASB reactor located at a confectionary factory (Ricolino, San Luis Potosí, México). Prior to inoculation both sludge samples were mixed at a ratio of 1:1 (v/v) and heated at 100 °C for 30 min to inactive hydrogen consuming microorganisms and to enrich spore-forming hydrogen-producing bacteria.

2.2. Mineral medium

The mineral medium composition was as follows (g/L): $NH_4H_2PO_4$, 45; Na_2HPO_4 , 119; K_2HPO_4 , 1.25; $MgCl_2 \cdot 6H_2O$, 1.0; $MnSO_4 \cdot 6H_2O$, 0.15; $FeSO_4 \cdot 5H_2O$, 0.25; $CuSO_4 \cdot 5H_2O$, 0.05;

Table 1 – Chemical composition of oat straw hydrolysates.

Sugar	Sugar composition in hydrolysate (mg/L)	
	Batch 1	Batch 2
Mannose	1124.5	1346.0
Xylose	1187.7	5813.9
Glucose	896.8	2002.1
Arabinose	814.4	1572.2
Galactose	824.1	565.6
COD (g/L _{hydrolysate})	15	35

COD: chemical oxygen demand.

$CoCl_2 \cdot 5H_2O$, 0.03; $Na_2MoO_4 \cdot 2H_2O$, 0.125; $ZnCl_2$, 0.0075. The pH of the mineral medium was adjusted to 5.5.

2.3. Oat straw hydrolysates

Oat straw used was commercially available (Forrajera Marquez Company, San Luis Potosí, México). A laboratory ball mill (Thomas Wiley, Model 4, Thomas Scientific, USA) was used to reduce straw particle size to an average of 2 mm. To obtain oat straw hydrolysates, the residue was dried at 60 °C and then heated at 90 °C per 2 h in an HCl solution at 2% (v/v). The hydrolysate was filtered through absorbent gauze cloth. The hydrolysate was characterized in terms of the type and concentration of sugars and chemical oxygen demand (COD). Table 1 shows the chemical characteristics of the oat straw hydrolysate.

2.4. Reactor experiments

Fig. 1 shows the schematic of the BF used in this study. The BF was made up of an acrylic cylinder divided into three equal sections. A volume of 783 mL of each section was filled with a mixture of perlite (average diameter of 2.4 mm, Perlita de La

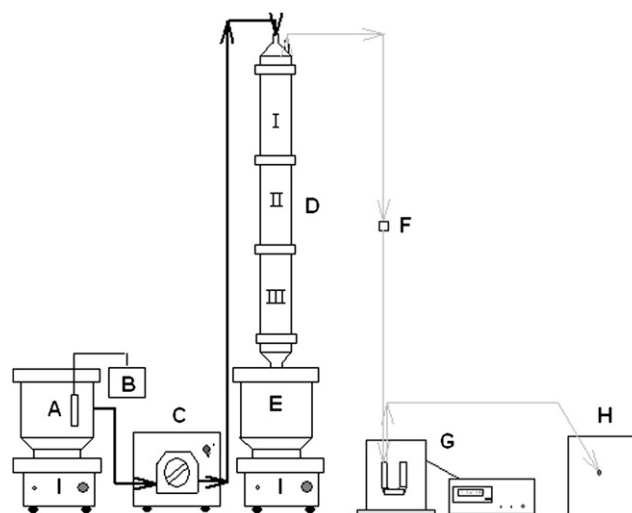


Fig. 1 – Biotrickling filter scheme A) Feeding tank, B) pH meter, C) Peristaltic pump, D) Bioreactor, E) Leaching tank, F) Gas sampling port, G) Wet gas meter, H) Tedlar bag, I) Magnetic stirrers. Roman numbers indicate the sections of the reactor.

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