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Biohydrogen production from pretreated corn cobs

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ABSTRACT

In this study, the co-fermentability of four different pretreated corn cob streams at different mixing ratios was assessed. The four streams, denoted DP, DS, HP, and HS, were: two dilute acid pretreatment comprising one purge and one squeeze and two high pressure autohydrolysis comprising one purge and one squeeze. The "Purge" stream was taken from the steam percolation reactor during cooling and the "Squeeze" stream was recovered from the cooked biomass with a pressing step. In addition, the impact of furfural and 5-hydroxymethylfurfural (HMF) on biohydrogen production potential was evaluated. The DP:DS mix at 50:50 by volume achieved the maximum H_2 yield of 265 (mL/gCOD sugars consumed). Furfural at concentrations of 0.21–1.09 g/L had no impact on H_2 production rates and yields and HMF was below the inhibitory threshold of 0.14 g/L. A positive correlation was observed between the monomeric-to-polymeric sugars ratio and H_2 production rates and yields.

Introduction

A wide variety of feedstocks and wastes that are rich in carbohydrate content have the potential to produce hydrogen using dark fermentation [1]. A number of studies have utilized real waste streams for biohydrogen production like sweet potato-starch residue [2], insoluble co-products of wheat starch food industry [3], sugarcane bagasse [4], thin stillage from bioethanol processing [5], and cassava stillage from ethanol processing [6].

Lignocellulosic biomass, of which two thirds are carbohydrate polymers of cellulose and hemicellulose [7] is the most abundant raw material. Corn cobs contain 32.3%–45.6% cellulose, 39.8% hemicelluloses-mostly pentosan, and 6.7%–13.9% lignin [8]. Cellulose is a linear polymer of cellobiose (glucose–glucose dimer) and upon hydrolysis yields free glucose molecules. Hemicellulose, on the other hand, consists mainly of xylose, arabinose, galactose, glucose, and mannose which are easily fermentable [9]. Prehydrolysis is required to convert carbohydrate polymers to fermentable monomeric sugars [7].

Xylose is the second most common product of saccharification of organics after glucose [10]. Linand Cheng [10] investigated mesophilic hydrogen production from xylose

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using a mixed anaerobic culture in both chemostat and batch bioreactors, and achieved hydrogen yields of 0.7 and 2.25 mol H_2/mol xylose, respectively, with the major observed VFAs being acetate, propionate, and butyrate, with butyrate as the major component. Danko et al. [11] observed a hydrogen yield of 1.98 mol H_2/mol substrate consumed for arabinose at a concentration 10 g/L using a mixed-culture anaerobic sludge and the soluble products released in addition to n-butyrate were formate, propionate, valerate, and ethanol. Cheng et al. [12] obtained a hydrogen yield of 1.12 mol H_2/mol xylose while de Sa et al. [13] achieved 1.88 mol H_2/mol xylose, both using mesophilic anaerobic sludge. Yokoi et al. [14] studied hydrogen production using a mesophilic facultative anaerobe, *Enterobacter aerogenes* strain HO-39 and, obtained hydrogen yields of 0.95, 0.98, and 2.16 mol H_2/mol-substrate for the monosaccharides galactose, and mannose as well as the disaccharide, maltose, respectively. In a more recent study, *E. aerogenes* IAM 1183 utilized xylose, galactose, and mannose mesophilically yielding 2.2, 2.35, and 2.62 mol H_2/mol substrate, respectively [15]. Ghosh and Hallenbeck [16] studied *Escherichia coli* strain DJT135 for mesophilic biohydrogen production from arabinose, galactose, maltose, and xylose, and achieved hydrogen yields of 1.02, 0.69, 0.72 and 0.57 mol H_2/mol-substrate, respectively.

Apart from carbohydrates and depending on the raw material and the pre-treatment applied, the resulting hydrolysates may contain substances such as furfural and HMF that could be potentially inhibitory to fermentation [17]. Furfural derivatives affect microbial growth by interfering with glycolytic and/or fermentative enzymes and also disturb the membrane integrity of diverse microorganisms, with concentrations as low as 1 g/L considered inhibitory [18]. Quéméneur et al. [18] assessed the impact of 1 g/L furfural and HMF concentrations on H_2 production from xylose at 5 g/L concentration by anaerobic digester sludge, and observed inhibition of H_2 production in terms of the duration of the lag phase, H_2 yield, and maximum H_2 production. In the aforementioned study, H_2 yields decreased from 1.67 mol H_2/mol xylose in the control (xylose-only) batch bottles to 0.45 (±0.10) mol H_2/mol xylose, and with no gas production from furfural or HMF when added as the sole carbon source at 1 g/L.

HMF compromises the cell membrane integrity, and intracellular sites are the primary inhibition targets [19]. Microorganisms are known to relieve the inhibitory effects of these furan compounds by metabolic pathway switching, thereby converting HMF and furfural to less toxic compounds, provided the initial concentrations are not beyond threshold levels [20]. Furfural is converted to furfuryl alcohol and furoic acid while HMF is converted to 5-hydroxymethyl furfuryl alcohol or 2,5-bis-hydroxymethylfuran [21–23]. Chemical potential fluctuations in the microenvironment, differences in the type and quantity of microorganisms, pH variations, and concentrations affect the metabolic pathways.

Co-fermentation of different organic residues has demonstrated enhanced hydrogen production in a number of studies suggesting synergistic and complementary effects *b* [24]. Some of the reported advantages of co-digestion are dilution of toxic compounds, improved nutrients balance, improved buffering capacity, and synergistic microbial effects [24]. Fangkum and Reungsang [25] studied the thermophilic co-digestion of xylose and arabinose at 2.5 g/L each concentrations using anaerobic mixed cultures, and obtained a maximum hydrogen yield of 2.59 mol H_2/mol-sugar consumed with 95% substrate degradation. Substrate degradation was observed to decrease with the increase in xylose/arabinose concentrations.

In light of the reported advantages of co-fermentation as well as limited literature on the impact of HMF and furfural on biohydrogen production, the main objectives of this study were to: a-evaluate the co-fermentability of four different pretreated corn cob streams at different mixing ratios; b-assess the potential inhibitory impact of furfural and HMF; and c-examine the impact of monomeric-to-polymeric sugars composition on H_2 yields and rates. This study examined the biodegradation of specific polymeric carbohydrates, that is, arabinose, xylose, mannose, galactose, and glucose.

Materials and methods

Seed sludge and substrate

Anaerobic digester sludge (ADS) was collected from St. Mary's wastewater treatment plant (St. Mary's, Ontario, Canada) and preheated at 70 °C for 30 min prior to use. Four different pretreated corn cob streams, for potential use in the bioethanol industry, were obtained from an industrial facility (Ontario, Canada) and used as substrates. Table 1 shows the characteristics of the four streams. Dilute Acid Pretreatment (DAP) and High Pressure Autohydrolysis (HPA) were used as a first stage pretreatment to facilitate the second stage pretreatment for hemicellulose solubilisation. Purge and Squeeze streams differ in their location in the cellulosic pretreatment process; where "Purge" is taken from a steam percolation reactor during cooling while "Squeeze" is recovered from the cooked biomass via pressing. The four streams are denoted henceforth as DP (dilute acid pretreatment – purge stream), DS (dilute acid pretreatment – squeeze stream), HP (high pressure autohydrolysis pretreatment – purge stream), and HS (high pressure autohydrolysis pretreatment – squeeze stream).

Batch setup

Batch anaerobic experiments were conducted in serum bottles with a liquid volume of 200 mL. Volumes of substrates and seed were calculated based on a substrate-to-biomass (S°/X°) ratio of 2 gCOD/gVSS using the following equation:

$$S^\circ/X^\circ = \frac{V_{sub}(L)*TCOD_{eq}\left(\frac{g}{L}\right)}{V_{seed}(L)*VSS_{seed}\left(\frac{g}{L}\right)}$$

where V_{sub} is the volume of substrate, V_{seed} is the volume of seed, and $TCOD_{eq}$ is the equivalent total chemical oxygen demand (TCOD) for different volumetric mixing ratios of the four streams (HP, HS, DP, and DS) as shown in Table 2. A total of 18 different mixing ratios for the four streams were tested with no replication. A control batch was prepared using ADS without any substrate. The initial pH for the mixed solution in