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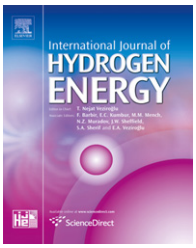

Biohydrogen production from apple pomace by anaerobic fermentation with river sludge

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ABSTRACT

The biological hydrogen (bio-H_2) production from apple pomace (AP) by fermentation using natural mixed microorganisms in batch process was studied under various experimental conditions. The river sludge was used as a seed after being boiled for 15 min. The results show that the optimal pretreatment for AP was to soak it in the ammonia liquor of 6% for 24 h at room temperature. An optimal fermentation condition for bio-H_2 production was proposed that the pretreated AP at 37 °C, the initial pH of 7.0 and the fermentation concentration of 15 g/l could produce a maximum cumulative H_2 yield (CHYm) of 101.08 ml/g total solid (TS) with an average H_2 production rate (AHPR) of 8.08 ml/g TS/h. During the conversion of AP into H_2, acetic acid, ethanol, propionic acid and butyric acid were main liquid end-products.

1. Introduction

High dependence on fossil fuels has led to serious energy crisis and environmental problems, so it is very urgent for the exploration of clean and renewable substitutes. Among all the alternative energy, hydrogen (H_2) has attracted more and more attention due to the characteristic of being clean, high efficient and renewable. Currently, H_2 can be generated by many methods, including thermocatalytic reforming of H_2-rich organic compounds, electrolysis of water and biological processes [1]. Among the methods, biological hydrogen (bio-H_2) production is found to be sustainable and environmental friendly [2]. Moreover, organic wastes can be used as fermentation substrates for bio-H_2 production, which facilitates both waste treatment and energy recovery. For the two biological routes, photosynthetic and fermentative H_2 production, the fermentative H_2 production seems more feasible for practical applications because it is rapid, simple and independent of weather condition [3].

The fermentative H_2 production mainly depends on temperature, pH and substrate concentration [4–7]. The temperature and pH are two important factors in biological fermentation process due to their effects on the substrate utilization, H_2 production and liquid end-product distribution as well as bacterial growth. At present, some investigators have reported the effect of temperature on the fermentative H_2 production using various natural mixed microorganisms such as cow dung compost and anaerobic digester sludge [8,9]. However, the detailed information regarding the effect of temperature on the fermentative H_2 production with river sludge as seed is still lacking. In addition, the reported optimal initial pH values are different for different cellulosic materials, varying from pH = 4.5 [9] for rice slurry, pH = 6.5 [10] for beer lees to 7.0 or 8.0 for wheat straw [8].

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Currently, substrates for the fermentative H_2 production mainly include simple sugars, starch and biomasses such as crops, agricultural and industrial wastes and cellulosic municipal solid wastes [11–14]. However, natural cellulosic materials cannot be used to produce H_2 directly because the cellulose polymers in the cell wall are intricately associated with lignin and hemicellulose. Therefore, cellulosic materials must be pretreated so as to remove lignin and hemicellulose, as well as to reduce cellulose crystallinity before utilizing them. Although there were many studies on the fermentative H_2 production from cellulosic materials [15–17], few investigations on H_2 production by fermentation from apple pomace (AP) were reported. In general, AP accounting for about 25% of fresh fruit weight is mainly composed of pericarp, core and pulp remains. In China, the yield of AP as a byproduct of juice extraction is more than 1 million tons, but only a small amount of AP is used for deep-processing, and the vast majority is not effectively utilized yet. In addition, AP is highly biodegradable and rich in sugars and fibres, its disposal as waste causes not only a serious environmental problem but also a huge loss of precious resources [18]. Therefore, it can be considered as a very potential substrate to produce H_2 by fermentation. The purpose of this work was to determine the optimal condition for the conversion of AP into H_2 by the river sludge. A series of batch experiments were conducted to investigate the effects of substrate pretreatments, initial pH, temperature and substrate concentration on the fermentative H_2 production.

2. Materials and methods

2.1. Pretreatment of substrate

Apple pomace (AP) used in this work was obtained from a juice-making factory of Xianyang city. Before analysis, AP was dried at 65 °C for 24 h. Its main components analyzed are as follows: reducing sugar 13.52, cellulose 16.91%, lignin 24.11%, and hemicelluloses 20.00%. There are still some other components, including moisture, pectin, mineral, vitamin C, crude protein, crude fat and so on [18]. The total solid (TS) content was 97.13% in this study.

Before being degraded by microorganisms, AP was pretreated by the following two methods: Method 1, AP was soaked in H_2SO_4 solution at room temperature for 12 h, or treated in H_2SO_4 solution by ultrasonic with a frequency of 25 kHz at various time, and then adjusted pH to 7.0 with dilute NaOH solution; Method 2, AP was first soaked in ammonia liquor at room temperature at various time, and then the solid was obtained by filtration and washed repeatedly with distilled water until the wash water reached pH 7.0. The above-obtained filtrate was concentrated at 50 °C to remove ammonia from the solution, subsequently, the above solid and concentrated filtrate were mixed to be as the fermentation substrate for the H_2 production. The ratio of solid to liquid was 0.1 g/ml for all pretreatments in this work.

2.2. Seed microflora

The seed used in this study was natural anaerobic activated sludge, which was obtained from the Bahe river of Xi'an city. Prior to use, the river sludge was boiled for 15 min to inhibit the bioactivity of methane-forming bacteria and enrich H_2-producing bacteria.

2.3. Batch experiments

The batch experiments were conducted with 150 ml three-necked flasks as reactors. In each run, the reactor was filled with 100 ml mixture of heat-pretreated sludge, substrate and nutrient stock solution. Then the reactor was sealed and incubated with continuous stirring at 120 rpm to ensure thorough mixing and facilitate the rapid diffusion of biogas. One liter of culture medium contained: peptone, 4000 mg; L-cysteine, 600 mg; NaCl, 2000 mg; KH_2PO_4, 2000 mg; $MgSO_4{\cdot}7H_2O$, 500 mg; $FeSO_4{\cdot}7H_2O$, 6 mg. The volume and composition of biogas were monitored once every time period. Only carbon dioxide and H_2 were detected from gas products. The liquor samples were taken for the volatile fatty acids (VFAs) and alcohols analysis after fermentation.

2.4. Analyses

The volume of biogas was measured by the water-displacement method in a measuring cylinder. The composition and proportion of biogas were analyzed by an on-line gas chromatograph (GC-SP-6890) with a thermal conductivity detector (TCD) and 3 mm inside diameter stainless-steel column packed with molecular sieve TDX-01. Argon was used as the carrier gas at the flow rate of 40 ml/min. The operational temperatures at the column oven, injection and detector were kept at 90, 130 and 130 °C, respectively. The liquid end-products were determined by a second gas chromatography (SP-6890) under the following conditions: column: 3 mm inside diameter stainless-steel column packed with polymer beads TDX-01, carrier gas: nitrogen (flow rate: 40 ml/min), detector: flame ionization detector (FID), column temperature: 170 °C, injection temperature: 200 °C, detector temperature: 200 °C.

3. Results and discussion

3.1. Effect of substrate pretreatment on H_2 production

3.1.1. Effect of H_2SO_4 pretreatment

Fig. 1 depicts the changes of cumulative H_2 yield (CHY) verse time at 37 °C, initial pH 6.0 and fermentation substrate concentration 20 g/l. It is apparent from Fig. 1 that the CHY for all the fermentation processes of AP increased rapidly with time and finally reached a maximum value. As shown in Fig. 1a, the CHY gradually increased with the increase of H_2SO_4 concentration in the range of 0–0.5% under the condition of soaking for 12 h, and a maximum cumulative H_2 yield (CHYm) of 69.74 ml/g TS was obtained at the H_2SO_4 concentration of 0.5%. While the CHY gradually decreased with the increase of H_2SO_4 concentration in the range of 0.5–1.0%, was only 48.39 ml/g TS at the H_2SO_4 concentration of 1.0%. As we know, a relatively higher H_2SO_4 concentration is conducive to the hydrolysis of substrate, however, when a much higher SO_4^{2-} anion was introduced into the culture medium, the growth of H_2-producing bacteria was also severely inhibited