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Two stage hydrogen production using maize stalk hydrolysate

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Abstract : Fermentative hydrogen production was combined with microbial electrolysis cell for the enhancement of hydrogen production from maize stalk hydrolysate. In the first phase fermentation was carried out in liquid medium by facultative bacterial strain isolated from soilutilizing maize stalkhydrolysate as carbon source. At the end of fermentation, the effluent was collected, and the fermentation end products were analysed. In the second stage, the fermentation effluent was used as feed for microbial electrolysis cell (MEC) for further hydrogen production. Anode of the MEC was a type A carbon cloth enriched with waste water inoculum and cathode was type B carbon cloth. MEC was operated under anaerobic condition by passing nitrogen gas and at applied voltages ranging from 0.3 to 0.8 V. By incorporating MEC, the overall hydrogen production increased by 2.19-fold.
Keywords : Two stage hydrogen production, maize stalk hydrolysate.

1. Introduction

Hydrogen produced from biological process is considered as the promising alternative to fossil fuels. But, dark fermentation which is commonly practiced can convert only 20-25% of the stoichiometrically available hydrogen and the rest end up as fermentation end products which cannot be further converted into hydrogen via fermentation. This process will be viable only when the hydrogen present in these end products is released. Electrohydrogenesis is such a method for the conversion of organic matter into hydrogen gas by bacteria with a small input of electrical energy. It hasalso emerged in recentyears as a promising technology for wastewater treatment[7]. Microbial electrolysis cell (MEC) operates in a manner like a microbial fuel cell with an additional voltage in the circuit to produce hydrogen as this process is thermodynamically unfavourable[10]. In an MEC the anode and cathode can either be separated by a membrane[9] or can be placed in a single chamber[1]. Bioelectrochemical microbes at the anode compartment oxidize the organic matter to CO_2, protons and electrons. These electrons reach the cathode through the external circuit, where it reduces water to form hydrogen[6,8]. A new advancement in MEC is the use of single chamber membrane free microbial electrolysis

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cells which not only simplifies the construction, operation and maintenance of MEC but also decreases the internal resistance thereby increasing the hydrogen production rate[3,5]. Microbial electrolysis in this study has been carried out with a single chamber membrane free MEC.

2. Material and Methods

Dried and powdered maize stalk was hydrolysed in autoclave using 1% sulphuric acid at 121 ^{o}C, 1.5 kg/cm^2 for 60 min with a solid to liquid ratio of 1:20. After hydrolysis, the solidresi due has been separated by filtration and the pH of the hydrolysate was adjusted to 7 using NaOH.For fermentative hydrogen production, volume of hydrolysate equivalent to 1 g of glucose has been used as the source of carbon. Fermentations were carried out in liquid medium with the following composition: malt extract,1.0 g/L; peptone, 5.0 g/L; yeast extract, 2.0 g/L; NaCl, 5.0 g/L and maize stalk hydrolysate (equivalent to 1 g of glucose).The total gas produced during the fermentation was estimated by water displacement method and the amount of hydrogen constituted in the total gas was determined using a gas chromatograph(AIMIL-NUCON 5765, Mumbai, India) equipped with a thermal conductivity detector. At the end of fermentation, the cells were separated from the fermentation broth by centrifugingat 5000 rpm for 10 min. The supernatant obtained were analysed for organic acids using HPLC(Shimadzu, Japan), which is equipped with 4 µm Hydro-RP column (250 ×4.6 mm) at ambienttemperature. Organic acids like oxalic, tartaric, formic, pyruvicand citric acid were quantified using an ultraviolet detector.The 500 mL glass bottles were used for MEC construction. Anode was made of Type A carboncloth (3.5 ×4 cm^2) and cathode was made of Type B carbon cloth (4 ×5 cm^2) and were separated by aJ-cloth (4 ×4 cm^2) (Hongqiang et al., 2008). Anodes used in the MEC were initially enriched withbacteria in a microbial fuel cell using sewage as inoculum. The inoculum was omitted from the MFC,once the output voltage reached reached a stable value above 0.1 V.

3. Results and Discussion

Facultative hydrogen producing bacteria isolated from the soil of maize stalk storage yard was used for fermentative hydrogen production. Fermentations were carried out at pH 7; temperature, 30^{o}C and with an inoculum size of 3%. Hydrogen production of 62.3 mL H_2/Lwas obtained at 48 hr andafter which only a slight increase was observed (Fig. 1). Thus, 48 hr was considered as the end offermentative hydrogen production.At the end of fermentation, the bacterial cells were separated from the fermentation effluent bycentrifugation. The supernatant collected on HPLC analysis revealed the presence of oxalic (4.7µg/mL), tartaric (3.1 µg/mL), formic (0.76 µg/mL), pyruvic (1.50 µg/mL) and citric acid (0.32µg/mL)(Table 1). The other common fermentation end products including acetic acid, ethanol, lactic acid, succinic acid etc were not analysed. The MEC reactor was fed with the fermentation effluent and wassparged with nitrogen gas for 10 min to maintain anaerobic condition. The anode enriched with microbial consortium was placed in the MEC with applied voltage in the range of 0.3 V to 0.8 V and the gases produced were collected in a sealed tube place at the top of the chamber. With increasing applied voltage, hydrogen production also increased from 19.23 mL H_2/L at 0.3 V to 74.29mL H_2/L at 0.6 V. Further increase in applied voltage resulted in a reduction in hydrogen production. Hydrogen gasproduction was observed right after the placement of anode and increased continuously up to the thirdday and no further increase were observed from the next day. A total gas collection of 483 mL/L with15.38% of H_2 (74.29 mL H_2/L) was observed after 68 hours of operation. After which the effluent from the MECwas analysed for the concentrations of organic acids. Consumption of organic acids in MEC were oxalic acid, 2 µg/mL; tartaric acid, 2.49 µg/mL; formic acid, 0.76 µg/mL; pyruvic acid, 0.67 µg/mL and citric acid, 0.2 µg/mL. Except formic acid, allthe other analysed acids were present though with a lesser concentration compared to that at the initialstage. The presence of methanogenic bacteria would have hindered the further hydrogen production.Checking for methanogenesis and incorporation of further batches of MEC might increase thehydrogen production. The presence of formic acid in the fermentation effluent andthe utilization of it in MEC for hydrogen production were reported previously (Elodie et al., 2009).Though the utilization of acetic acid, ethanol, succinic acid, lactic acid, formic acid, and sodiumacetate (Chen and Logan, 2007; Douglas and Logan, 2008; Hongqiang et al., 2008; Elodie et al., 2009)was described earlier, but that of oxalic, tartaric, pyruvic and citric acids were not reported previously.

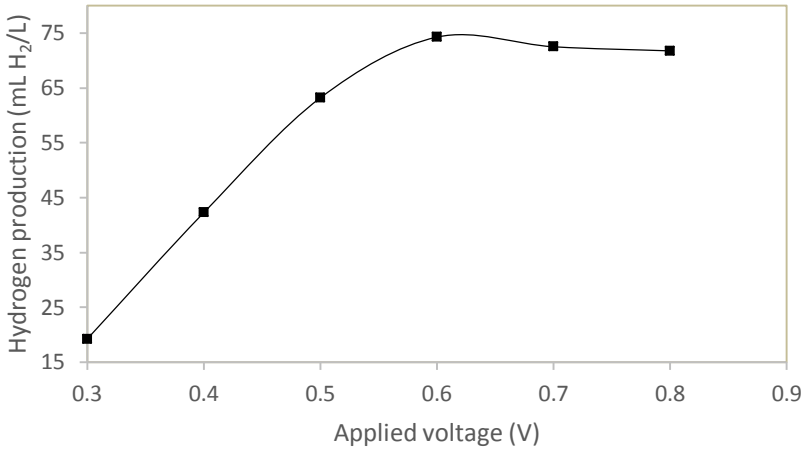

Figure 1. Hydrogen production profile in single chamber MEC as a function of applied voltage

4. Conclusions

` Facultative bacterial strain isolated from soil produced 62.3 mL H_2/L under fermentative conditions utilizing the cheap lignocellulosic substrate maize stalk. An applied voltage of 0.6V was found to be optimum for hydrogen production in the single chamber microbial electrolysis cell with a maximum hydrogen production of 74.29 mL H_2/L. The total hydrogen production obtained by the incorporation of fermentation with a single chambermicrobial electrolysis cellwas found to be 136.59 mL H_2/L.

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