INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–5

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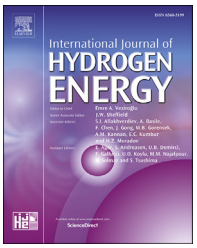

Mesophilic and thermophilic photo-hydrogen production from micro-grinded, enzyme-hydrolyzed maize straws

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ARTICLE INFO

Article history:
Received 4 April 2017
Received in revised form
9 May 2017
Accepted 10 May 2017
Available online xxx

Keywords:
Maize straw
Photo-fermentation
Biohydrogen
Enzymatic hydrolysis
Activation

ABSTRACT

Photo-fermentative is an endothermic reaction driven by light energy to overcome the energy barrier. This communication conducted photo-fermentation hydrogen tests with micro-grinded, enzyme-hydrolyzed maize straws considering the effects of broth temperature ranging 28.2–54.5 °C. The hydrogen production rate was first increased with broth temperature, peaked at 39.6 °C, and then decreased at higher temperature range. The photo-fermentative process can be approximated as a catalytic reaction with positive activation energy and positive activation entropy, an endothermic, entropy-driven complexation process.

Introduction

Waste-to-energy is an active research field with emphasized publication [1–3]. Photofermentative hydrogen production is a process that can convert organic substances to H_2 and CO_2 with the input of light energy [4,5]. The hydrogen yields of photofermentative pathway is shown to be higher than those of dark fermentative pathway [6,7]. To convert lignocellulosic waste to photo-hydrogen is one of the environmental friendly pathway for clean energy development of sustainable society [8].

Temperature affects photofermentative reaction rates. In photo-fermentation tests, the temperature of broth can increase with time because of the energy gain from incident light and the thermal effects by incorporated reactions [9]. In

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http://dx.doi.org/10.1016/j.ijhydene.2017.05.077
0360-3199/

outdoor cultivation the broth temperature can be much higher than the surrounding temperature. Assuming that the photo-hydrogen fermentation reaction can be described by a first-order reaction:

$$\frac{dC_A}{dt} = -kC_A = -k_0 e^{-\frac{E_a}{RT}} C_A \quad (1)$$

where C_A is the substrate concentration (mol/L); t is the reaction time (s); k is the rate constant (s^{-1}), k_0 is the frequency factor (s^{-1}), R is the gas constant (=8.314 J/mol-K), T is temperature (K), and E_a is the activation energy (J/mol). Then the reaction rate will be increased with temperature with a positive activation energy, E_a.

This study conducted fermentative hydrogen production test from micro-grinded, enzyme-hydrolyzed maize straws over 28.2–54.5 °C. The activation energy from the tests was estimated and discussed.

Material and methods

Materials

Maize straw, which were from Zhengzhou City, China with elemental compositions of 39.0% C, 6.2% H, 42.4% O, were used as the substrate. The samples were micro-grinded with a LG-02 grinder (Hangming Co., Zhengzhou, China) to particle size 53–61 μm. The micro-grinded samples were treated with cellulase (CAS No. 9012-54-8; Solarbio Co., Beijing, China) in 0.05 M sodium citrate buffer. Other pretreatment details are available in Ref. [8].

Reactor setup

Photofermentative hydrogen production tests were conducted with the biological consortium HAU-M1 that is described in Refs. [10,11]. The reactor setup was modified from that used in Ref. [12]. Briefly, 500-mL photo-reactors were fed with the hydrolyzate (with 10 g/L reduced sugar, or 0.057 M glucose equivalent) and the HAU-M1 with light sources located at the reactor sides. The temperatures in the reactor were monitored using thermocouples linked to multi-channel recorder. The testing time was 168 h.

Analytical methods

The surface illumination intensity was measured by LX1010B intensity meter (Shinbou Sci., Shenzhen, China). The hydrogen concentration of collected sample was measured by a GC-16B gas chromatograph (PerkinElmer, MA, USA) thermal conductivity detector (TCD) and 5A column. The carrying gas for the GC was 45 mL/min nitrogen.

Results and discussion

Photo-fermentation tests

In the fermentation tests, the temperatures in the reactor evolved with time (Fig. 1a). The reactor temperature reached steady states at >24 h testing. Also, the four temperature readings showed no significant differences, indicating that the temperature in the fermenting broth was uniform. Fig. 1b shows the temperature differences between that at reactor center a fermenting broth minus that of the same broth but without inoculum. The broth temperature showed rapid increase in the first 8 h, then the difference decayed to less than one degree after 24 h testing. The above results confirmed that the present photo-fermentation tests over 24–168 h can be assured as conducted at a prescribed isothermal environment.

The hydrogen production rate using 53–61 μm samples with consortium HAU-M1 at 2500 lux and pH 7 were shown in Fig. 2. The hydrogen production principally occurred during 48–68 h of test, hence the tests were performed at isothermal environment. The hydrogen production rate showed 39.6 °C > 48.5 °C > 35.6 °C > 54.5 °C > 28.2 °C, suggesting that the hydrogen production rate was increased when temperature was increased from 28.2 to 39.6 °C, and was then decreased with temperature till 54.5 °C.

Temperature effects

The Gibbs free energy changes for photo-fermentation from glucose to H_2 and HCO_3^- at pH 7 was close to zero at 25 °C and was decreased with increasing temperature (Fig. 3), suggesting that the photo-fermentation reaction favors high temperature environment. Fig. 3 also reveals the free energy changes for dark + photo-fermentation two-stage process for comparison sake: the dark fermentation is more favorable thermodynamically but the subsequent photo-fermentation is highly undesirable that needs extra driving force to make it occurred.

The enthalpy changes for photo-fermentative hydrogen production ($C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2$) reactions are positive, suggesting an endothermic reaction. Hence, the negative Gibbs free energy change is contributed heavily by very positive entropy change. The photo-fermentative hydrogen production is therefore an entropy-driven process. But the light energy is needed to overcome the energy barrier E_a.

Fig. 4 shows the semi-log plot for maximum hydrogen production rate versus reciprocal of temperature for the photo-fermentative hydrogen tests. As expected, the data were divided into two regimes, right with positive and left with negative E_a regime based on Eq. (1). The calculations showed that the consumed chemical oxygen demand to hydrogen was less than 7% of the fed quantity in hydrolyzate, hence the substrate concentration in the broth can be regarded constant over the testing period. Restated, the negative slope indicated in Fig. 4 can be used to estimate the activation energy. The result is $E_a = 28.4$ kJ/mol. This value is lower than 87.9 kJ/mol for *Citrobacter intermedius* [13], 38.3 kJ/mol for *Rhodopseudomonas palustris* P4 [14], 67.3 kJ/mol for *Enterbacter aerogenes* [15] 42.9 kJ/mol for Citrobacter sp. Y19 [16], and 53.8 kJ/mol for *Enterobacter cloacae* IIT-BT 08 [17], and 47.4 kJ/mol for *E. cloacae* IIT DM-11. The reference activated energy for cell growth is 54–71 kJ/mol [18]. The pre-exponential factor indicates the fraction of reactants that possess sufficient energy to overcome the E_a

Please cite this article in press as: Hu J, et al., Mesophilic and thermophilic photo-hydrogen production from micro-grinded, enzyme-hydrolyzed maize straws, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.05.077