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Potential use and the energy conversion efficiency analysis of fermentation effluents from photo and dark fermentative bio-hydrogen production

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ABSTRACT

Effluent of bio-hydrogen production system also can be adopted to produce methane for further fermentation, cogeneration of hydrogen and methane will significantly improve the energy conversion efficiency. Platanus Orientalis leaves were taken as the raw material for photo- and dark-fermentation bio-hydrogen production. The resulting concentrations of acetic, butyric, and propionic acids and ethanol in the photo- and dark-fermentation effluents were 2966 mg/L and 624 mg/L, 422 mg/L and 1624 mg/L, 1365 mg/L and 558 mg/L, and 866 mg/L and 1352 mg/L, respectively. Subsequently, we calculated the energy conversion efficiency according to the organic contents of the effluents and their energy output when used as raw material for methane production. The overall energy conversion efficiencies increased by 15.17% and 22.28%, respectively, when using the effluents of photo and dark fermentation. This two-step bio-hydrogen and methane production system can significantly improve the energy conversion efficiency of anaerobic biological treatment plants.

1. Introduction

Given its high energy density and lack of pollution emission when combusted, hydrogen has been recognized as the ideal alternative energy to fossil fuels (Zhang et al., 2017a; Kumar et al., 2015). Biological hydrogen production, with its mild processing conditions, abundant raw material sources, and low energy consumption, has attracted the attention of various researchers (Singh and Wahid, 2015; Urbaniec and Bakker, 2015).

Biological hydrogen production mainly includes photo and dark fermentation (Chandrasekhar et al., 2015). Photosynthetic bacteria (PSB) utilize several small-molecule volatile acids and monosaccharides in the fermented liquid, such as acetic acid, pyruvic acid, and butyric acid, as organic substrate to produce hydrogen (Pere and Nimalakhandan, 2010; Mizuno et al., 2000). Whereas, dark-fermentation bacteria decompose macromolecular organic matter into organic acids and alcohols (Barca et al., 2015; Li et al., 2010). The decomposition process provides energy and reducing power for the growth of dark-fermentation bacteria, removal of cumulative electrons, and quick release of hydrogen.

Broadly speaking, the bio-hydrogen production process is an intermediate stage of methane production by anaerobic digestion; hence, the utilization rate of substrates is low. Owing of this, a certain amount of volatile fatty acids ramains in the effluent at the end of the fermentative process, which results in low energy conversion efficiency. Direct discharge of fermentative effluents causes environmental pollution (Cheng et al., 2010; Xie et al., 2008). Ozmihic and Argun investigated bio-hydrogen production by the photo fermentation of dark-fermentation effluent from ground wheat starch. The content of volatile fatty acids in the dark-fermentation effluent decreased significantly during the photo-fermentative reaction (Ozmihci and Kargi, 2010; Argun et al., 2008). Therefore, dark-fermentation effluent can be effectively utilized as the substrate for photo fermentation bio-hydrogen production (Silva et al., 2015; Dahiya et al., 2015). The effluent can also be utilized as a carbon source for the culture of microbes (Chi et al., 2011). Combined dark- and photo-fermentation bio-hydrogen production has been demonstrated by several studies (Tawfik et al., 2014; Rai et al., 2014). Ghimire et al. (2016) used dark-fermentation effluent as the substrate to produce hydrogen from photo-fermentation, and then poly-β-hydroxybutyrate (PHB), resulting in 80% COD removal.

In recent times, single-stage processes that are a hybrid of dark and photo fermentation are gaining attention. First, dark-fermentation bacteria consume complex organic substrates, and then the volatile fatty acids byproducts are utilized by PSB. Temperature, pH, and effluent rate all have significant influence on hydrogen production; the total hydrogen output under optimum conditions increase by up to four times (Zagrodnik and Laniecki, 2015; Ngoma et al., 2011). Yeshanew et al. (2016) integrated the systems of continuously stirred tank reactor (CSTR) and anaerobic fixed bed reactor (AFBR) to evaluate the biohythane (bio-H_2+CH_4) yield from food waste; HRT and effluent

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recirculation rate were investigated, and optimal parameters were obtained. Short HRT was found good for bio-hydrogen yield, and recirculation of the AFBR effluent provided alkalinity to the whole system, which maintained the pH in a suitable range for the growth and metabolism of the hydrogen producing bacteria. Several factors such as a nature of substrate, microbial consortium, and reactor configuration influence the process of bio-hydrogen and subsequent bio-methane production from waste biomass by dark fermentation technology (Liu et al., 2013). Methanogenic archaea grow slowly and are a vulnerable microbial group. Given that methanogenic archaea can utilize volatile fatty acids as substrates, the methane production process can be the final stage in the anaerobic fermentation process (Aydin et al., 2015). Some scholars have conducted the bio-hydrogen and bio-methane production process from cow dung, waste water, starch-rich biomass, and etc. (Intanoo et al., 2014; Reungsang et al., 2012; Zhu et al., 2008). However, little research has been done using fallen leaves (Song et al., 2010). As the main street tree in China, the annual leaves production of Platanus Orientalis reaches ten-million tones. The common treatment methods of fallen leaves are landfill, burn, and compost. The energy consist in the leaves is not being fully utilized, and the combustion of leaves may cause the environmental pollution. Given that fallen leaves consist of cellulose and hemicellulose, which can be utilized for fermentation (Zhang et al., 2014, 2017b; Li et al., 2017). Hence, using fallen leaves as the raw material for fermentation helps recycle waste biomass, bringing about clear environmental benefits.

When combining the diverse fermentative pathways, the organic matter in the fermented liquid can be maximally utilized, and the energy conversion efficiency can be improved greatly. Arimi et al. (2015) found the production of methane to have higher energy recovery than that of hydrogen. Hence, it can be suggested that a process that combines fermentative bio-hydrogen and bio-methane production has the potential for the highest energy recovery (Nasr et al., 2012). Moreover, the combination of dark fermentation and methanogenesis improves the energy conversion efficiency to 23.1% (Cheng et al., 2012). Hence, in this study, for the efficient utilization of biomass and maximum energy conversion efficiency, Platanus Orientalis leaves were taken as the substrate to evaluate the energy conversion efficiency of bio-methane and bio-hydrogen coproduction. We believe that understanding the energy recovery from this fermentation process will enhance the overall energy conversion efficiency of anaerobic biological treatment plants.

2. Materials and methods

2.1. Fermentation ingredients

In this study, Platanus Orientalis leaves were collected from the sidewalks at the Wenhua Road Campus of Henan Agricultural University. The leaves were naturally air dried and crushed through a 40-mesh sieve before use. The determination of lignocellulosics components of Platanus Orientalis leaves was conducted by NREL method (Sluiter et al., 2012). The composition of the leaves was 32.51% cellulose, 19.65% hemicellulose, 30.13% lignin, and 17.71% other components, with a 91.5% volatile solids mass fraction.

2.2. Inoculum

(1) Hydrogen-producing photosynthetic bacteria: HAU-M1 mixed bacteria (Lu et al., 2016) were prepared by staff from the Key Laboratory for Renewable Energy, New Materials, and Equipment of the Ministry of Agriculture. When the strain concentration reached 1.25 ± 0.02 g/L (OD_{660} 1.2), the bacterial mixture was used in hydrogen production experiments. The incubation time was 48 h.

Growth medium: NH_4Cl, 0.5 g; $NaHCO_3$, 2 g; K_2HPO_4, 0.2 g; CH_3COONa, 4 g; $MgSO_4{\cdot}7H_2O$, 0.2 g; NaCl, 2 g; yeast extract, 1 g; distilled water, 1 L.

Hydrogen production medium: NH_4Cl, 0.4 g/L; $MgCl_2$, 0.2 g/L; yeast extract, 0.1 g/L; K_2HPO_4, 0.5 g/L; NaCl, 2 g/L; glucose, 10 g/L; sodium glutamate, 3.5 g/L.

(2) Dark-fermentation bacteria: Our bacteria produced acclimated active anaerobic granules, with 18.25% total solids (TS) and 32.82% volatile solids (VS).

Growth and hydrogen production medium: NaCl, 2 g; K_2HPO_4, 1.5 g; $MgCl_2$, 0.2 g; CH_3COONa, 2 g; peptone, 4 g; yeast extract, 1 g; distilled water, 1 L.

(3) Methane-producing bacteria: Bacteria were obtained through the fermentation of a mixture of cow dung and straw in an anaerobic environment and subsequent filtration through a 0.5 mm sieve.

2.3. Major reagents and equipment

Sulfuric acid, calcium hydroxide, potassium hydroxide, and other reagents used in the experiments were all analytical grade (AR); an Agilent HP8453 spectrophotometer (Agilent Technologies, California, USA); a biochemical incubator (SPX-150B, Tianjin Taisite Instrument Co. Ltd.); a pH meter (Delta 320, Guangzhou Derun Instrument Technology Co.); and a 6820 GC-14B gas chromatograph produced by Agilent Co. were also used.

2.4. Fermentation device

The fermentation device used is shown in Fig. 1.

The reactor shown in Fig. 1 is used for photo, dark bio-hydrogen production process and methane-producing fermentation by using effluents derived from hydrogen production process (fermentation). The processes of photo- and dark fermentation were controlled by a light switch.

2.5. Raw material pretreatment

Platanus Orientalis leaves were soaked in 4% H_2SO_4 at a solid-liquid ratio of 1:20 (g:mL). The reaction mixture was mixed well, and the reaction was performed at 120 °C for 120 min. After treatment, distilled water was used to repeatedly wash the sample until the filtrate was neutral. The sample was air-dried at 45 °C and then sealed in a container for storage.

2.6. Procedures

A total of 5 g of pretreated raw material was placed in a 250 mL Erlenmeyer flask, and 100 mL citric acid-sodium citrate buffer (pH 4.8) was added to produce an enzyme load of 150 mg/g leaves. After the flask was sealed, the reaction mixture was maintained in a 50 °C water bath for 48 h.

(1) Photofermentative hydrogen production: after enzymolysis, the reaction mixture was titrated to a neutral pH with 50% KOH solution,

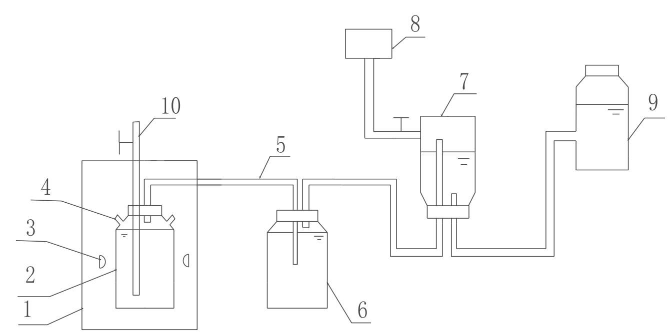

Fig. 1. Schematic diagram of fermentation device (1. Incubator 2. Bioreactor 3. Filament lamp 4. Charging port 5. Airway tube 6. Gas purifier 7.Gas bottle 8. Gas chromatograph 9. Water seal 10. Argon input).