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Production of hydrogen, ethanol and volatile fatty acids from the seaweed carbohydrate mannitol

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HIGHLIGHTS

- Mannitol can be efficiently fermented by AFB to produce H_2 and SMPs.
- The theoretical maximum specific H_2 yield is 615.4 mL H_2/g mannitol (5 mol/mol).
- The optimal specific H_2 yield achieved was 224.2 mL H_2/g mannitol (1.82 mol/mol).
- The overall energy conversion efficiency achieved was 96.1% via fermentation.
- Energy production was dominated by H_2 (17%), butyric acid (38%) and ethanol (34%).

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ABSTRACT

Fermentative hydrogen from seaweed is a potential biofuel of the future. Mannitol, which is a typical carbohydrate component of seaweed, was used as a substrate for hydrogen fermentation. The theoretical specific hydrogen yield (SHY) of mannitol was calculated as 5 mol H_2/mol mannitol (615.4 mL H_2/g mannitol) for acetic acid pathway, 3 mol H_2/mol mannitol (369.2 mL H_2/g mannitol) for butyric acid pathway and 1 mol H_2/mol mannitol (123.1 mL H_2/g mannitol) for lactic acid and ethanol pathways. An optimal SHY of 1.82 mol H_2/mol mannitol (224.2 mL H_2/g mannitol) was obtained by heat pre-treated anaerobic digestion sludge under an initial pH of 8.0, NH_4Cl concentration of 25 mM, NaCl concentration of 50 mM and mannitol concentration of 10 g/L. The overall energy conversion efficiency achieved was 96.1%. The energy was contained in the end products, hydrogen (17.2%), butyric acid (38.3%) and ethanol (34.2%).

1. Introduction

1.1. Hydrogen as a source of renewable energy

Excessive use of non-renewable fossil fuels, such as petroleum and coal, is problematic due to finite fossil fuel resources, and for the state of the environment (Sambusiti et al., 2015; Wei et al., 2013). Hydrogen is considered as a promising alternative, due to its clean combustion product (i.e., water) and high energy density by mass (i.e., 142 kJ/g of higher heating value) (Argun and Kargi, 2011; Guwy et al., 2011). The major source of hydrogen production (steam reforming of natural gas) is a mature technology but is soured from fossil fuel (Xia et al., 2015b). A second mature source (water electrolysis) converts electricity to hydrogen; the sustainability of the produced hydrogen is dependent on the sustainability of the electricity generation.

1.2. Hydrogen via anaerobic fermentation

In contrast, hydrogen production via anaerobic fermentation can be considered a green source of energy and can be renewable and sustainable (Matsumura et al., 2014; Saady, 2013; Sambusiti et al., 2015). The soluble metabolic products (SMPs) derived from fermentation can be used for the production of biofuels and biochemicals (Guwy et al., 2011; Motte et al., 2015). The substrate choice is critical in establishing the green credentials of hydrogen fermentation (Sambusiti et al., 2015).

Abbreviations: AFB, anaerobic fermentative bacteria; HPE, hydrogen production efficiency; FAN, free ammonia nitrogen; MUE, mannitol utilisation efficiency; SHY, specific hydrogen yield; SMP, soluble metabolic product; TAN, total ammonia nitrogen; VFA, volatile fatty acid; VS, volatile solids.

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1.3. Seaweed as a source of hydrogen

Marine seaweed (macroalgae) biomass, which may be derived from mass cultivation and/or natural algal blooms, offers an attractive option for biohydrogen production. Seaweed has many advantages over conventional biomass from food crops and cellulosic materials. These include: high biomass productivity; growth in a marine environment (not requiring arable land); and lack of lignin and hemicellulose which allows easy fermentation and minimises requirement for substrate pre-treatment (Matsumura et al., 2014; Wang et al., 2013; Wei et al., 2013). Nevertheless, there are challenges in hydrogen fermentation using seaweeds as substrates.

1.4. Suitability of carbohydrates in seaweed for hydrogen production

Carbohydrates are the most important components for hydrogen production; monomers derived from carbohydrates involve the basic fermentation reactions (Sambusiti et al., 2015; Xia et al., 2015a). The carbohydrate monomers derived from land-based biomass are dominating by glucose and xylose, hydrogen production from which, has been extensively investigated (de Vrije et al., 2007; Fang and Liu, 2002; Lin and Cheng, 2006; Pierra et al., 2014; Salerno et al., 2006; Tien Anh et al., 2012; Wang et al., 2009). However, carbohydrate monomers, such as mannitol, may dominate seaweed (Wei et al., 2013) and have a remarkable effect on the performance and potential of hydrogen production from seaweed (Xia et al., 2015a). Mannitol ($C_6H_{14}O_6$) is a typical seaweed carbohydrate, which can be 20–30% of dry weight in brown seaweeds (Matsumura et al., 2014). Mannitol is a simple sugar alcohol with high solubility in water, however, it is difficult to ferment particularly in an anaerobic environment; this makes it a challenge for biohydrogen production (Wang et al., 2013).

1.5. Components of seaweed, which adversely affect hydrogen production

Seaweeds usually have much higher sodium content as compared with land-based biomass, due to their origin in the marine environment (Matsumura et al., 2014). A high sodium concentration may adversely affect the hydrogen fermentation process (Kivisto et al., 2010; Lee et al., 2012; Pierra et al., 2014; Sambusiti et al., 2015; van Niel et al., 2003; Zheng et al., 2005). Furthermore, the high content of proteins (7–20% of dry weight) in seaweeds may produce excess ammonia/ammonium during anaerobic degradation (Wei et al., 2013). The total ammonia nitrogen (TAN) level is considered another important parameter in hydrogen fermentation (Salerno et al., 2006; Sambusiti et al., 2015; Wang et al., 2009).

1.6. Objectives

Hydrogen fermentation using mannitol as a substrate is rare in the literature (Heyndrickx et al., 1991; Matsumura et al., 2014); no literature was found used mixed anaerobic inoculum. Moreover, the impacts of sodium and TAN concentrations on hydrogen production from mannitol have yet been investigated. The use of the seaweed carbohydrate mannitol as a model substrate for fermentative hydrogen production would be helpful for the understanding of the fermentation process treating seaweeds and beneficial for the further process optimisation. Thus the objects of this study are to:

- Calculate the theoretical specific hydrogen yields (SHYs) of mannitol fermentation via different metabolic pathways.
- Assess the impacts of parameters (initial pH, sodium concentration, TAN concentration and mannitol concentration) on the fermentation process.
- Analyse overall energy conversion.
- Assess further SMP utilisation approaches.

2. Methods

2.1. Inoculum

The mixed anaerobic fermentative bacteria (AFB) were separated from the anaerobic digestion sludge collected from a farm digester treating dairy slurries, food wastes and grease wastes. The sludge was pre-treated in an autoclave at 100 °C for 30 min to suppress the non-spore-forming hydrogen consumers (e.g., methanogenic microorganisms), then was acclimated three times (3 days each time) to activate spore-forming AFB (e.g., *Clostridium butyricum*) for subsequent fermentation (Xia et al., 2015a). The acclimation medium was modified according to a previous study as follows (all values per litre): mannitol, 20.0 g; tryptone, 3.0 g; yeast extract, 1.0 g; NaCl, 3.0 g; K_2HPO_4, 2.5 g; $MgCl_2$, 0.1 g; $FeCl_2$, 0.1 g; L-cysteine, 0.5 g; vitamin liquid, 10.0 mL; and trace element liquid, 10.0 mL. The compositions of the vitamin and trace element solutions were descripted in a previous study (Cheng et al., 2012). The contents of total solids and volatile solids (VS) in the inoculum were 7.0% ± 0.4% and 4.0% ± 0.2%, respectively.

2.2. Fermentation processes

Batch fermentation tests were conducted in triplicate in two AMPST II systems (Bioprocess Control, Sweden). This system mainly includes a sample incubation unit (600 mL glass bottles placed in a water bath), a carbon dioxide fixing unit (120 mL glass bottles with 3 M NaOH solutions) and a gas volume measuring device (gas tipping device equipped with pressure and temperature sensors).

30 mL of acclimated AFB and 270 mL of basal medium were added to a glass bottle. The total fermentation volume was 300 mL. The initial pH was measured by a pH metre (Jenway 3510, UK) and adjusted by using 6 M NaOH or 3 M HCl solutions.

In pH trials, the initial compositions of the fermentation liquor were as follows (g/L): mannitol, 10; NH_4Cl, 1.34 (or 25 mM); NaCl, 2.93 (or 50 mM); K_2HPO_4, 2.5 g; $MgCl_2$, 0.1 g; and $FeCl_2$ 0.1 g. The initial pH was tested in 7 steps (4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 ± 0.05). A control run was operated without mannitol under an initial pH of 7.0 ± 0.05, whereas other experimental parameters were set the same as experimental runs.

In TAN concentration trials, the initial compositions of the fermentation liquor were as follows (g/L): mannitol, 10; NH_4Cl in the range 0–26.75 (or 0–500 mM); NaCl, 2.93 (or 50 mM); K_2HPO_4, 2.5 g; $MgCl_2$, 0.1 g; and $FeCl_2$ 0.1 g. The NH_4Cl concentration was tested in 7 steps (0, 15, 25, 50, 100, 200 and 500 mM). The initial pH was set as 8.0 ± 0.05. A control run was operated without mannitol under initial NH_4Cl concentration of 1.34 g/L (or 25 mM).

In sodium concentration trials, the initial compositions of the fermentation liquor were as follows (g/L): mannitol, 10; NH_4Cl, 1.34 (or 25 mM); NaCl in the range 0–58.5 (or 0–1000 mM); K_2HPO_4, 2.5 g; $MgCl_2$, 0.1 g; and $FeCl_2$ 0.1 g. The NaCl concentration was tested in 8 steps (0, 25, 50, 100, 200, 400, 600 and 1000 mM). The initial pH was set as 8.0 ± 0.05. A control run was operated without mannitol under initial NaCl concentration of 2.93 g/L (or 50 mM).

In mannitol concentration trials, the initial composition of the fermentation liquor were as follows (g/L): mannitol in the range 0–40 g/L; NH_4Cl, 1.34 (or 25 mM); NaCl, 2.93 (or 50 mM);