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Unexpectedly low biohydrogen yields in co-fermentation of acid pretreated cassava residue and swine manure

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ABSTRACT

Co-fermentation of carbon-rich and nitrogen-rich feedstocks with suitable carbon to nitrogen (C/N) ratios is commonly considered as a viable way to enhance biological hydrogen production. In this study, cassava residue (C/N ratio = 29.1) and swine manure (C/N ratio = 8.6) were mixed and subject to microwave-assisted acid hydrothermal pretreatment. The resulting hydrolysates were used for subsequent dark hydrogen fermentation. However, the mixture with a C/N ratio of 15.1 resulted in the lowest hydrogen yield potential of 107.8 mL/g volatile solid (VS). Comparatively, the mono-fermentation of cassava residue exhibited the highest hydrogen yield potential of 145.6 mL/g VS and a peak hydrogen production rate of 8.2 mL/g VS/h. The modified Gompertz model was employed for kinetic analysis, and suggested that the lag-phase time and peak time of hydrogen fermentation exhibited a significantly positive linear correlation with increased C/N ratios. Reducing sugars analysis indicated that pretreatment of mixed cassava residue and swine manure led to a decrease of total sugar yield by 7.2–10.5% due to the Maillard reactions between hydrolyzed sugars and amino acids. A reaction mechanism based on glucose and arginine was proposed to elucidate the Maillard interactions between carbonyl group (−C=O) and amino group (−NH_2), which was responsible for the overall sugar loss. The findings of this study suggested that pretreatment for mixed carbohydrate-rich and protein-rich feedstocks needs to be optimised to avoid unexpected fermentable sugars loss.

1. Introduction

Gaseous biofuels (such as biomethane and biohydrogen) derived from biomass will play a vital role in future renewable and sustainable energy supplies [1–4]. Hydrogen is an ideal and clean energy carrier with many economic and environmental benefits, such as its high energy density (higher heating value of 142 MJ/kg) and clean combustion product (water) [5–7]. Biological hydrogen production from various renewable feedstocks has been identified as more environmental friendly and less energy intensive, as compared to thermo-chemical and electro chemical processes [8,9].

The characteristics of feedstocks are a key factor for fermentative hydrogen production. Wet organic wastes (such as agricultural residues, livestock manures and municipal solid wastes) are considered as excellent feedstock options because they are inexpensive and readily available [10–13]. In addition, these wastes are usually rich in carbohydrates, which are recognized as the main fermentable component for hydrogen production. However, biological fermentation suffers from the intrinsic recalcitrance of cellulosic feedstocks owing to their complicated structure of high-molecular weight [14–17]. Prior to fermentation, these feedstocks need to be effectively pretreated in order to improve the subsequent biofuel production. When subjected to mechanical pretreatment, the crystal structure of cassava residues can be significantly destroyed, resulting in increased amorphization and decreased crystallinity [18]. Pretreating cassava stems with ionic liquid [Emim]OAc can also reduce cellulose crystallinity and lower lignin content [19]. Acidification pretreatment was shown to improve biohydrogen yield by 36.1% from cow manure [20]. Among the various pretreatment methods, acid hydrothermal pretreatment is considered to be one of the most promising technologies that can efficiently improve sugar release from biomass [21]. However, one major concern about acid pretreatment is the possible formation of fermentative inhibitors (such as furfural and 5-hydroxymethylfurfural). The increase of acid pretreatment severity (high temperature and/or high acid concentration) results in an increase in formation of inhibitors, which possess significant inhibitory effect on fermentative microorganisms. The degradation of these inhibitors (typically containing aldehyde group) in fermentation usually involves the reduction reaction converting

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aldehydes into alcohols. This process requires a considerable consumption of reducing chemicals, such as nicotinamide adenine dinucleotide (NADH). The depletion of NADH by inhibitors has been proposed as the possible inhibition mechanism for hydrogen fermentation [22].

Suitable C/N ratios during fermentation play an important role in contributing to efficient hydrogen production. Due to the variation in carbohydrate and protein contents of different feedstocks, the mixture of carbohydrate-rich and protein-rich feedstock offers a solution to adjust C/N ratios for efficient biological fermentation. Although proteins have lower hydrogen production potentials than carbohydrates, they are necessary to balance the C/N ratio for bacteria growth [23]. It was reported that the highest hydrogen yield was achieved at the substrate composition of 87:13 (food waste: sewage sludge, VS basis) [24]. By co-digestion of carbohydrate rich cassava stillage with protein rich cassava excess sludge (waste generated after biological treatment of cassava), an increase of hydrogen yield of 46% was achieved as compared to cassava stillage alone [25]. Co-substrates addition allowed optimization of C/N ratio and enrichment of the hydrogen-producing bacteria. Kim et al. suggested an optimal C/N ratio of 25 in co-fermentation of rice straw and sewage sludge [26]. Similarly, Xia et al. concluded that C/N molar ratio of 25.3 gave the highest dark hydrogen yield from mixed biomass of cassava starch and algae [27].

Cassava can widely grow in barren areas subject to drought, and is an important energy crop for starch production in China. According to statistics from the Food Agricultural Organization (FAO) of the United Nations, the annual worldwide cassava production was approximately 268 million tons in 2014 (http://www.fao.org/home/en/), indicating that a large amount of cassava residue could be generated in cassava-based industries. The worldwide swine stock in 2014 was reported as over 985 million heads (http://www.fao.org/home/en/). The huge amount of manures produced requires a suitable disposal technology. The quantities and compositions of cassava residue and swine manure suggest a major resource for biological and renewable hydrogen generation. There are numerous research papers which focus on pretreating biomass and optimizing C/N ratios for effective hydrogen production [24,25,28,29]. The comparison of dark hydrogen yields from various wastes in reported literature is shown in Table 1. The reported hydrogen yield from acid pretreated cassava reached 342 mL/g $COD_{reduced}$ [30], which was much higher than those (from 14.0 to 53.3 mL/g VS) from untreated cassava stillage [25,31–33]. Co-fermentation of manure with fruit–vegetable resulted in a higher hydrogen yield of 126 mL/g VS, which was ascribed to the suitable C/N ratio and enhanced buffer capacity [34].

However, research on co-fermentation of cassava residue and swine manure for hydrogen production was not found in the literature. Moreover, there is a gap in research on the interactions between carbohydrates and proteins during pretreatment (such as acid hydrothermal) of mixed cassava residue and swine manure and the impact of this pretreatment on subsequent hydrogen fermentation. The innovation of this study is the investigation of the interactions of sugars and amino acids during microwave-assisted acid hydrothermal pretreatment and assessment of the impacts on subsequent hydrogen fermentation. The detailed objectives of this study are to: (1) Evaluate the production of reducing sugars and amino acids after microwave-assisted acid hydrothermal pretreatment of mixed cassava residue and swine manure; (2) Assess the effects of mix ratios on subsequent hydrogen production kinetics, soluble metabolic products formation, and overall energy conversion efficiencies; (3) Reveal the reaction mechanism of sugars and amino acids during microwave-assisted acid pretreatment.

2. Materials and methods

2.1. Inoculum and feedstock

Activated sludge was collected from a mesophilic anaerobic digester mainly treating swine manure slurry. The collected sludge was heat treated at 100 °C for 30 min to inactivate methanogens, and then was acclimatized three times to harvest mixed spore-forming hydrogen-producing bacteria as detailed previously [27]. The acclimatized sludge was used as inoculum for dark hydrogen fermentation.

Cassava residue was obtained from a bioethanol plant located in Guangxi Province, China. Swine manure was sampled from a swine farm in Zhejiang province, China. The samples of cassava residue and swine manure were oven-dried at 105 °C, and powdered to 0.02 mm mesh size. The pulverized samples were stored at 4 °C for further use.

2.2. Experimental design

2.2.1. Pretreatment and enzymatic hydrolysis

Microwave-heated acid hydrothermal pretreatment has been proven to be effective for hydrogen and subsequent methane fermentation of cassava residue in a previous study by the authors [35]. In this study, the pretreatment was conducted in a microwave digestion system (Shanghai Yiyao WX-4000, China). A total amount of 5 g of mixed biomass at different mass ratios (dry solid basis, namely mass ratios of cassava residue to swine manure = 5:0, 4:1, 3:2, 2:3, 1:4, and 0:5, respectively) was added into polytetrafluoroethylene reactors. Subsequently 100 mL of diluted sulfuric acid (1.0% v/v) was mixed into the reactors. The sealed reactors were then placed in the microwave digestion system and underwent heat pretreatment at 140 °C for 15 min. The followed enzymatic hydrolysis of pretreated biomass was performed in flasks. The pH of mixed biomass solution was adjusted to 4.5 using 6 M NaOH solution. *Trichoderma reesei* cellulase (Shanghai Boao Biotechnology Corp., China) was added to the solution at 5 wt% of the original biomass. The flasks were then sealed and placed in a shaker at 120 r/min for 120 h at 45 °C.

Table 1
Comparison of dark hydrogen yields from various wastes in reported literature.

Feedstock	Pretreatment	Temperature (°C)	Reactor configuration	Hydrogen yield (mL/g VS)	Reference
Cassava stillage	/	37	CSTR[a]	14.0	[31]
Cassava stillage	/	60	CSTR[a]	76.0	[32]
Cassava stillage + cassava excess sludge	/	60	CSTR[a]	57.8	[25]
Cassava stillage	/	37	Batch	35.3	[33]
Cassava stillage	/	60	Batch	53.3	[33]
Cassava pulp hydrolysate	121 °C with H_2SO_4	35	Batch	342 mL/g $COD_{reduced}$	[30]
Cow manure	/	36	Batch	13.3	[20]
Cow manure	Boiled with 0.2% HCl for 30 min	36	Batch	18.1	[20]
Swine manure	/	35	Batch	68.5[b]	[53]
65% swine manure with 35% fruit-vegetable waste	/	55	Semi-continuously fed reactor	126	[34]

[a] CSTR = Continuous stirred tank reactor.
[b] Calculated based on the reported data.