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Hydrogen and Methane Production from Starch Processing Wastewater by Thermophilic Two-Stage Anaerobic Digestion

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Abstract

A two-stage thermophilic fermentation for hydrogen and methane production from wastewater of cassava rice and corn starch at different concentration (5,10 and 15 g/L) was studied. The hydrogen production from cassava starch at concentrations of 5 g/L gave the highest hydrogen yield and followed by cassava starch at a concentration 10 g/L, rice starch at concentrations of 15 g/L. The hydrogen and methane yields from cassava starch processing wastewater by two-stage was 81.5 L H₂ kgCOD⁻¹ and 310.5 L CH₄ kgCOD⁻¹, respectively with total energy yield of 13363 kJ kgCOD⁻¹. Mixed hydrogen and methane (biohythane) production was 9.51 L biogas l⁻¹ with containing of 55% CH₄, 11% H₂ and 34% CO₂.

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1. Introduction

Energy is an important part of sustain human life, which most of the energy used comes from fossil fuels such as coal, crude oil and natural gas and when fossil fuels are burned, carbon dioxide and other pollutants generated. Hydrogen as an alternative energy to get attention. Since it is clean energy environmentally friendly and has a by-product of combustion is water [15]. In addition, hydrogen has a higher energy value compared to the fuel the currently used is value of energy of hydrogen fuel is more than about 3 – 4 times more than coal. Hydrogen production can done in several ways, such as Steam

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reforming (Coal gasification), Water electrolysis and Thermochemistry, but energy for producing high compared to biological production (Biohydrogen) is used in the production of hydrogen energy and cost less than other methods. Anaerobic fermentation by microorganisms which can bring waste of carbon is a component that is used as a food source and waste utilization. Thailand population increases rapidly, causing the expansion of social and industrial increasing cause the demand for more energy. Moreover the demand for food has increased the amount of waste generated by processing greater such as the waste from the processing of cassava industry (cassava chips industry, cassava pellets and cassava starch), 60% of cassava production to use the human food, 27.5% for animal feed and 12.5% use the other side [16]. cassava starch processing wastewater is containing organic in a high carbohydrate.

Two-stage anaerobic digestion (AD) process has often been reported as a viable way to produce biohydrogen and biomethane from a wide range of organic materials, [2] where the digestion process has been divided up into an acidification stage and a methanogenic stage [17]. In the first acidogenic process, organic polymers, such as carbohydrates, proteins, and lipids, are converted to volatile fatty acids (VFAs) hydrogen and CO₂ in the first stage under slightly acidic (pH~5.0 – 6.0), VFAs are then converted to methane in the subsequent methanogenic step from the first reactor at a more neutral acidity (pH~7.0 – 8.0) [7, 18]. This work aims to investigated hydrogen production and methane of cassava, rice, cone starch and energy recovery from thermophilic two-stage anaerobic digestion.

2. Methodology

2.1 Feedstock

The synthetic wastewater from three starch typical of Cassava, Rice and Corn starch was prepared according to O-Thong et al. (2011) [4] with different concentrations (5, 10 and 15g/L). Total solid (TS) and Volatile solid (VS) of Cassava, Rice and Corn starch were 0.87, 0.82 and 0.63 g/L respectively.

2.2 Biochemical hydrogen potential (BHP) and Biochemical methane potential (BMP)

The BHP and BMP of POME were identified in batch assays under thermophilic conditions, as described previously by Giordano et al. (2011) [3]. The two-stage batch thermophilic fermentation of starch processing wastewater was carried out in 500 mL serum bottle with a working volume of 200 mL. 160 mL of wastewater and 40 mL of inoculums was added into serum bottles in hydrogen fermentation in the first stage. The headspace was replaced with nitrogen gas and incubated for 4 days. When the biological hydrogen production ceased, 80 mL of methane inoculum was added into 120 mL hydrogen effluent and incubated at thermophilic condition for 45 days in order to evaluate the CH₄ production in the second stage.

2.3 Analytical methods

The reactors were manually mixed every day during the first 7 days and every 2 days for the rest of the experimental duration and then maintained at static conditions. Biogas production was determined through the use of the water replacement method.⁵ Biogas composition in the headspace of the vials was monitored by GC-TCD. The gas produced by the negative control bottles with inoculum was subtracted from the actual gas produced of each treatment. Liquid samples were also taken from the culture before and at the end of each experiment for analyzing the composition of soluble metabolites including pH, total solid (TS), volatile solid (VS), volatile fatty acids (VFA) and total carbohydrates. pH was measured using pH-meter. TS and VS were measured according to the standard methods [9] total carbohydrates were determined by anthrone-sulfuric acid methods [10] at 620 nm using a spectrophotometer U-2001 (Hitachi, Japan).

2.4 Microbial community analysis

Polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE) [6] was used to study microbial community structure in the hydrogen production stage methane production stage as pervious described by Kongjan et al. (2010) [7]. Most of the bands were excised from the gel and re-amplified. After re-amplification, PCR products were purified and sequenced by Macrogen Inc. (Seoul, Korea). Closest matches for partial 16S rRNA gene sequences were identified by database searches in Gene Bank using BLAST.

2. Results

A two-stage thermophilic fermentation for hydrogen and methane production from starch processing wastewater was investigated. The biohydrogen and biomethane potential from cassava starch processing wastewater were 68.3-81.5 L H₂ kgCOD⁻¹ and 250.3-310.5 L CH₄ kgCOD⁻¹, respectively.

Table1. Hydrogen production from cassava corn rice processing wastewater at difference starch concentration

	Starch concentration (g/L)	Input (gCOD)	Remain (gCOD)	Consumed (gCOD)	Removal (%)	H ₂ yield (LH ₂ kgCOD ⁻¹)	Initial pH	Final pH	H ₂ production (LH ₂ Lsubstrate ⁻¹)
Cassava	5	34.5	9.4	25.1	72.8	81.5	6.48	6.15	0.4
	10	39.7	11.8	27.9	70.3	81.2	6.32	5.74	0.9
	15	44.9	15.9	29.0	64.6	68.3	6.33	5.85	1.1
Corn	5	34.5	9.4	25.1	72.8	74.3	6.32	5.83	0.4
	10	39.3	11.9	27.4	69.7	69.2	6.42	5.83	0.7
	15	44.4	15.9	28.5	64.2	48.8	6.30	5.78	0.7
Rice	5	34.0	9.8	24.2	71.2	79.8	6.41	5.68	0.4
	10	38.7	12.3	26.4	68.2	48.2	6.31	5.91	0.5
	15	30.6	16.3	14.3	46.7	72.0	6.28	5.25	1.1

The biohydrogen and biomethane potential from corn starch processing wastewater were 64.2-72.8 L H₂ kgCOD⁻¹ and 261.4-289.9 L CH₄ kgCOD⁻¹, respectively. The biohydrogen and biomethane potential from rice starch processing wastewater were 48.2-79.8 L H₂ kgCOD⁻¹ and 280-288 L CH₄ kgCOD⁻¹, respectively. The hydrogen production from cassava starch at concentration of 5 g/L gave the highest hydrogen yield and followed by cassava starch at a concentration 10 g/L, rice starch at concentrations of 15 g/L (Table 1,2). The study of Zhang et al. (2003) studied the production of hydrogen at high temperature, pH and different concentration of starch. The maximum hydrogen yield of 92 ml/g of starch added at a concentration of starch increased the yield of hydrogen lower down [11]. This is consistent with Hasyim et al. (2011) demonstrated at a concentration of starch higher yield hydrogen decreased. This may be caused by factors such as the degradation of starch incomplete. The experimental results of the VFA after hydrogen production at the highest concentration (15 g L⁻¹) of starch, each with the VFA and the concentrations of starch decreased VFA was low, [12] and the study of Kim et al. (2011) have studied the production of hydrogen from Tofu processing waste at high temperatures. Found that after hydrogen production of volatile fatty acids occur, such as acetic acid and butyric acid. [13] A study by Azbar et al. (2009) have studied the production of hydrogen from cheese whey, showed that hydrogen is volatile fatty acid concentrations were 118-27,012 mgL⁻¹, and the effect of hydrogen fermentation pH decreased from 6.30 - 6.48 to 5.25 - 5.78. The microorganisms are capable of producing hydrogen is stopped [14]. The COD removal of starch processing wastewater from two-stage hydrogen and methane production was

46.7-88.3%. Cassava starch processing wastewater shown the best hydrogen and methane production. The hydrogen and methane yields from cassava starch processing wastewater by two-stage was 81.5 L H₂ kgCOD⁻¹ and 310.5 L CH₄ kgCOD⁻¹, respectively with total energy yield of 13363 kJ kgCOD⁻¹. (Fig.2) Mixed hydrogen and methane (biohythane) production was 9.51 L biogas l⁻¹ with containing of 55% CH₄, 10% H₂ and 35% CO₂. Hydrogen reactor was dominated with hydrogen producing bacteria of *Thermoanaerobacterium thermosaccharolyticum*, while acetoclastic *Methanoculleus* sp. was the dominant methanogen in methane reactor (Fig.3). Two-stage process for biohythane production could be efficiently for energy recovery from starch processing wastewater.

Table2. Methane production from hydrogen effluent of cassava corn rice processing wastewater at difference starch concentration

Starch concentration (g/L)	Input (gCOD)	Remain (gCOD)	Consumed (gCOD)	Removal (%)	CH ₄ yield (LCH ₄ KgCOD ⁻¹)	Initial pH	Final pH	CH ₄ production (LCH ₄ L-substrate ⁻¹)	
Cassava	5	9.4	2.3	7.1	75.5	310.5	7.44	7.58	2.7
	10	11.8	2.4	9.4	79.7	303.7	7.33	7.62	3.4
	15	15.9	2.4	13.1	84.9	250.3	7.47	7.65	3.9
Corn	5	9.4	2.4	7.0	74.5	289.9	7.40	7.60	2.6
	10	11.9	2.5	9.4	78.9	308.0	7.34	7.64	3.4
	15	15.9	2.4	13.5	84.9	261.4	7.46	7.62	4.2
Rice	5	9.8	2.2	7.6	77.6	280.3	7.52	7.60	2.6
	10	12.3	2.0	10.3	83.7	288.7	7.53	7.63	3.6
	15	16.3	1.9	14.4	88.3	287.2	7.10	7.66	4.2

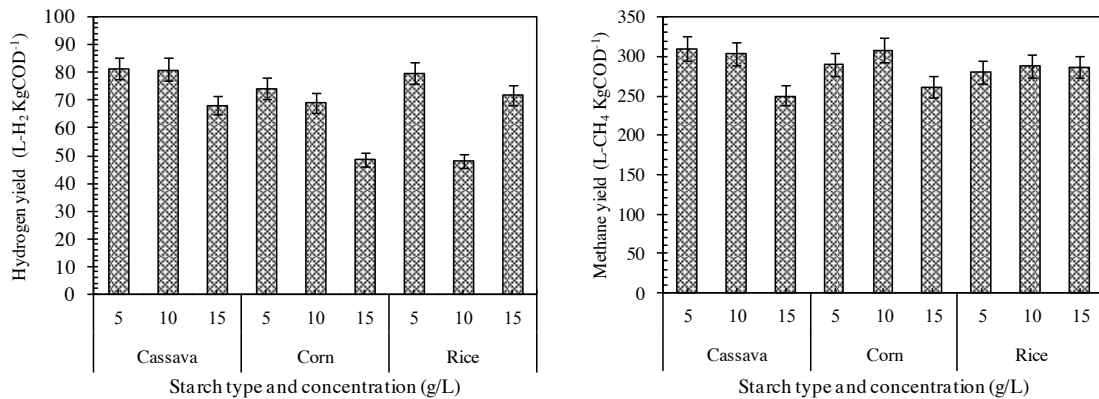


Fig.1. Hydrogen yield and methane yield from two-stage thermophilic anaerobic digestion of cassava, corn and rice starch processing wastewater.

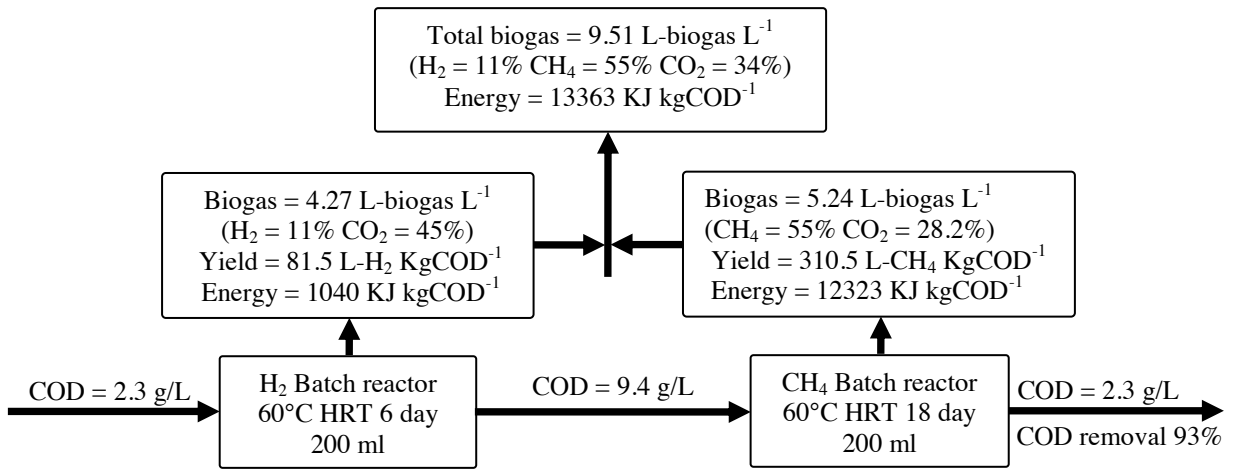


Fig.2. Mass and Energy balance in the two-stage anaerobic process for hydrogen and methane production

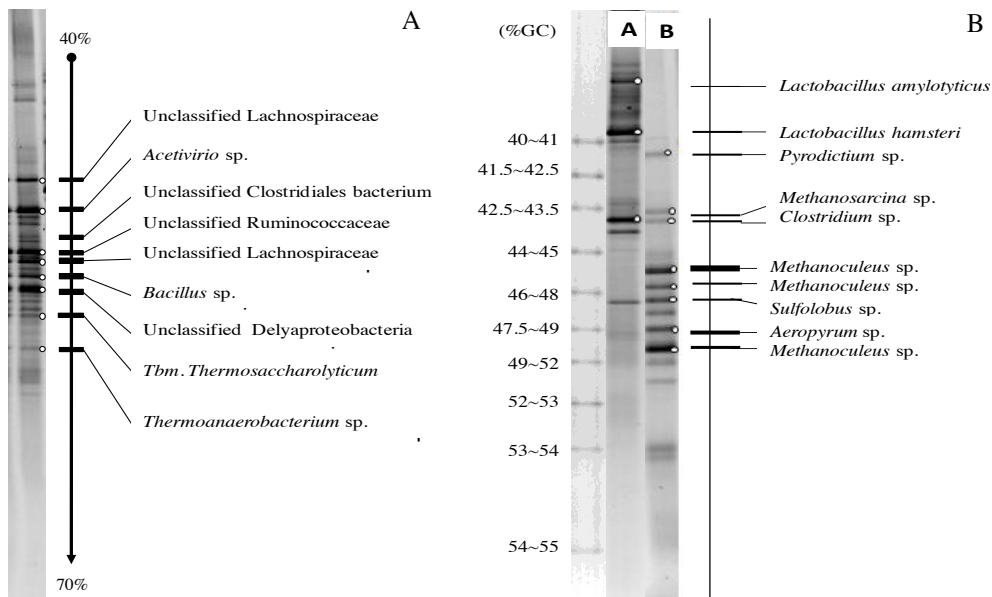


Fig.3. DGGE profile of 16S rRNA gene fragments. The fragments were PCR-amplified from total DNA extracted of hydrogen production stage (A) and methane production stage (B).

Conclusion

A two-stage thermophilic fermentation for hydrogen and methane production from wastewater of Cassava Rice and Corn starch at different concentration (5, 10 and 15 g/L). The hydrogen and methane yields from cassava starch processing wastewater by two-stage was 81.5 L H₂ kgCOD⁻¹ and 310.5 L CH₄ kgCOD⁻¹, respectively with total energy yield of 13363 kJ kgCOD⁻¹. Mixed hydrogen and methane (biohythane) production was 9.51 L biogas l⁻¹ with containing of 55% CH₄, 11% H₂ and 34% CO₂.

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