HYDROGEN PRODUCTION CHARACTERISTICS BY THERMOPHILIC ANAEROBIC SOLID STATE FERMENTATION PROCESS WITHIN THE WASTES

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SUMMARY: This study used cow manure (CM) as its source of hydrogen producing bacteria, and sewage sludge and food waste as its organic substrate. In a constant temperature experiment, the temperature control variables for bacteria screening were set between 50℃ and 75℃, separated by 5℃ increments. From this series, six thermophilic genera of bacteria were generated and each patch was subjected to 80 hours of thermophilic anaerobic fermentation at its respective constant temperature. The results were as follows: 60 ℃ series had a noticeable second peak growth period; its highest hydrogen yield was 56.75%; meanwhile, the specific hydrogen yield and specific hydrogen conversion rate were relatively high, 39 mL-H_2/g-VS and 4.00 g-H_2/g-H of VS%, respectively. In addition to these aforementioned high rates, the conversion, concentration, and fermentation process featured advantages such as a lack of need for outside-cultured hydrogen bacteria, rapid hydrogen production, pH stability, and low organic acidic liquidity. Lastly, organic waste was found to produce hydrogen by means of thermophilic anaerobic solid-state fermentation. This direction of research is worthy of further investigation and analysis.

1. INTRODUCTION

Hydrogen, with the characteristics of high thermal energy conversion and cleanliness, is recognized as the best alternative to fossil fuels (Kapdan et al., 2006; Lee et al., 2008). However, the vast majority of hydrogen either is chemically or physically comes from fossil fuels, e.g. steam reforming or partial gasification. These processes make hydrogen very expensive to

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produce, and harm to environmental externalities such as global warming and acid rain (Wen et al., 2009; Corbo et al., 2009; Vijayaraghavan et al., 2006; Sivaramakrishna et al., 2009). In this context, the search for a neutral renewable energy source is essential to new energy development.

Comparatively, biological hydrogen production is more cost efficient and does not require additional energy resources. For instance, anaerobic fermentation of hydrogen production does not require complex technology or equipment, which can be conducted so long as the fermentation requirements are satisfied. However, at present, this method is both time-consuming and inefficient (Gustavo et al., 2009; Lee et al., 2009). The key to a breakthrough is discovering how to use organic wastes as raw materials, produce hydrogen through biological pathways, and then obtain inexpensive environmental-friendly renewable energy. This breakthrough must address how to shorten the lag phase of growth, and increase production, conversion, and concentration rates. If successful, this method will not only improve waste recycling, but also benefit the economy and environment.

This study used various CM bacterial species for the fermentative hydrogen production source of organic waste. These included thermophilic (45-60°C), extremely thermophilic (≧60°C), and other symbiotic bacteria with hydrogen producing qualities (Sompong et al., 2008; Yokoyama et al., 2007; Liu et al., 2008). Using complex biological substances in organic waste matter as the raw material, and temperature as the screen factor, this study implemented a thermophilic solid-state fermentation hydrogen-producing experiment, which could overcome the limit of degradation rate during organic anaerobic digestion. The setup was designed to prevent compounds from further acidically dividing into volatile fatty acid solutions that produce a concomitant of NH_3, CO_2, H_2S, and other by-products. The organic wastes included undissolvable organic matter, high-molecular compounds (e.g. lipids, polysaccharides, proteins, and nucleic acids), and internally soluble organic substance (e.g. amino and fatty acids). After organic acid and ethanol had been further acetated, the corresponding complex hydrogen bacterial activities of thermophilic and extreme thermophilic bacteria produced acetic acid, CO_2, and H_2. Thermophilic fermentation was employed to inhibit methane bacteria from splitting acetate into methane, and 0.1N NaOH absorbed CO_2. These measures effectively controlled CO_2 as a receptor and H_2 as an electron supplier, avoiding further CH_4 derivation (Chen et al., 2008; Gomez et al., 2009; Lise et al., 2008).

For the basic experiment, this study focused on the aforementioned key technology. Using CM, sewage, and non-greasy food waste to establish the prerequisite conditions of thermophilic anaerobic solid-state fermentation. Both the hydrogen yield and conversion effectiveness of conversion of hydrogen atom to hydrogen molecule (hydrogen gas) of biomass were determined (Ren et al., 2009; Roy et al., 2009). The goal was for the organic ingredients in the waste material to be converted into organic waste substrate, and overcome the requirements of large reactor for traditional wet anaerobic fermentation. Additionally, the need for pre-sterilization treatment, bacteria cultivation, insuppressible bacteria methane production, and low substrate conversion also required resolution.

2.MATERAL AND METHODS

2.1 Substrate

CM 25 wt% and sewage sludge 50% were dehydrated to below 85% water content, then simulated non-greasy food waste 25 wt% (components contained smashed potatoes 25 wt%, fruit 40 wt%, vegetables 25 wt %, bread 8 wt%, and paper 2 wt%) was added. The three components were proportionally mixed into organic waste substrate.

Table 1 - Analysis of Substrate component.

Item	Sewage sludge	CM	Food waste
Moisture content (%)	78.9	77.3	77.5
Ash (%)	11.4	16.8	1.1
Combustible (%)	9.6	5.9	21.4
C (%)	5.14	3.18	8.14
H (%)	1.38	0.81	4.28
O (%)	1.81	1.21	6.47
N (%)	0.73	0.42	1.25
S (%)	0.54	0.27	1.25
Glucose-COD(g/L)	1	--	86

As the component analysis in Table 1 shows, during the fermentation period, the source of growth nutrients for thermophilic hydrogen producing bacteria came from biomass. Using anaerobic decomposition, hydrogen atoms from the organic ingredients were converted into hydrogen molecules (hydrogen gas), thus yielding a thermophilic anaerobic solid-state fermentation hydrogen production system.

2.2 Thermophilic solid-state batch fermentation hydrogen production system

Batch fermentation was adopted throughout the experiment. A reactor was designed with a 2.5-liter capacity for its round bottom type of fermentation tank. The top cover had one large and two small inlets. With its connecting rod inserted deep into the tank's testing bottle, the large inlet was accessible for an agitator device. The rod stirred evenly at 150 rpm. Meanwhile, the two small inlets separately measured pH changes and gas production in the bottle. The gas production inlet was connected to a plastic tube that led to a gas-liquid separating device designed for carbon dioxide separation. The segregation apparatus contained 0.1N sodium hydroxide. The plastic tube was first connected to a gas-sampling device. With a gas-tight syringe, 1μL of gas was extracted for chromatography analysis to detect biogas production and calculate its hydrogen content. Finally, using the exhaust gas water collection method, a plastic tube was linked to a 5.8-liter body of water to calculate gas production.

A fermenter aided in temperature control and maintenance. In order to suppress the production of light fermentation bacteria, a black lightproof cloth covered the entire fermentation unit. Once the bottle of implanted matrix was seated inside the fermenter, nitrogen gas was blown into the bottle for more than three minutes before being quickly sealed shut to ensure anaerobic conditions.

The aforementioned mix of sewage sludge, CM, and non-greasy food waste was mixed into a 2-liter continuous-stirring reactor. At a constant stirring speed, six different series of water baths were established using constant temperatures of 50 ℃, 55 ℃, 60 ℃, 65 ℃, 70 ℃, and 75 ℃.Figure 1 shows the batch thermophilic anaerobic dark fermentation hydrogen production process, research framework, and procedures. The pH and temperature changes were monitored throughout the experiment.

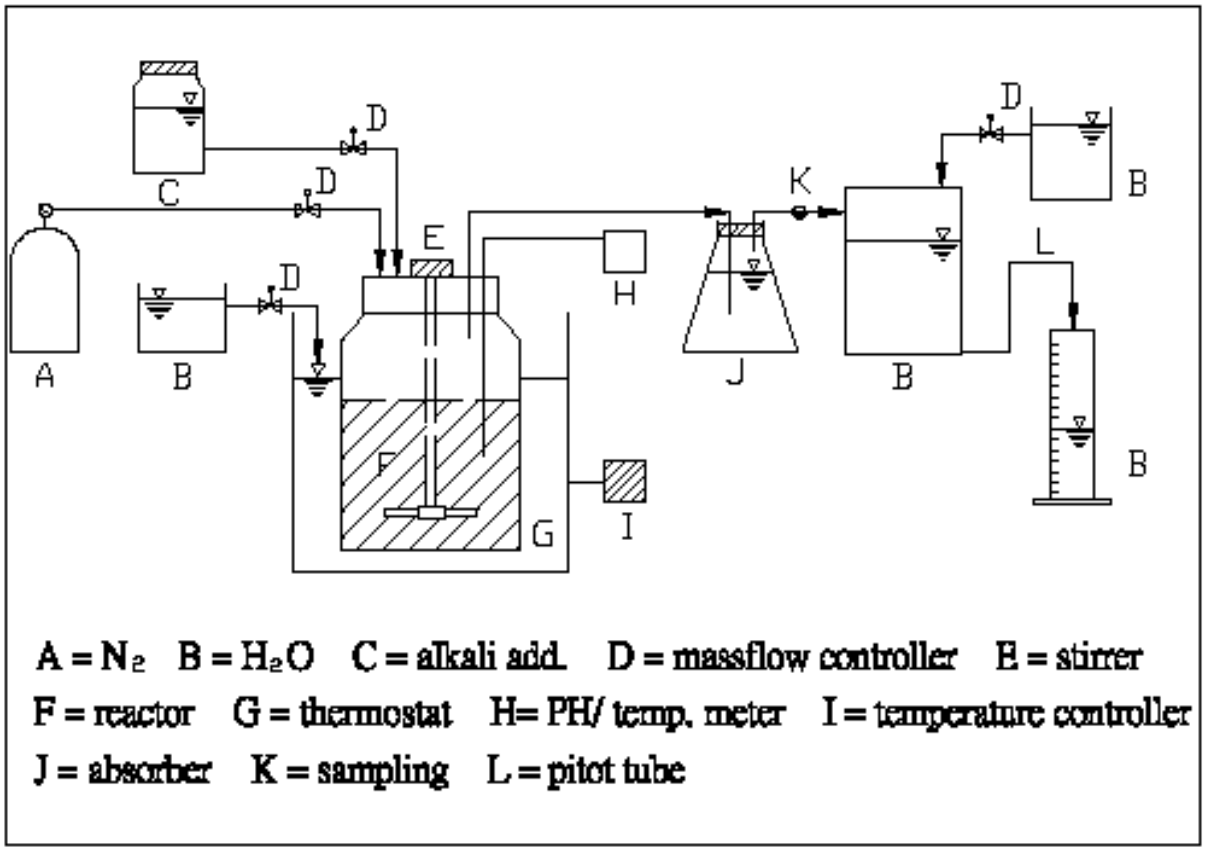

Figure 1. Experiment set-up apparatus.

The method exhaust gas water collection was adopted to evaluate the volume of biogas. Gas chromatography confirmed the hydrogen yield and its amount as a percentage of total biomass was calculated and recorded on a batch growth curve. Based on analysis, the hydrogen production experiments were compared to optimal operation conditions.

2.3 Analysis

A thermal conductivity detector (TCD) was built from a 2m × 5mm stainless steel column gas chromatography (China Chromatography, 9800 type) filled with Porapak Q (80/100 mesh). It compared the waveform position of the sample biogas with standard hydrogen peaks, confirming that hydrogen was produced. The proportions of hydrogen in biogas were calculated according to its waveform area (Fan et al., 2004). The temperature of the injection hole, fermentation tank, and detector were 200℃, 70℃, and 200℃. Nitrogen was used as the carrier gas with 1.5 kg/cm^2 gas pressure. The pH value inside the fermentation tank was displayed on a PH-208 digital microcomputer.

2.4 Specific hydrogen yield and specific hydrogen conversion rate (Li et al., 2008)

The “specific hydrogen yield "and "specific hydrogen conversion rate" be calculated the biomass hydrogen production.

$$Biomass\ \ dry\ \ weight\ = Batch\ \ of\ \ nongreasy\ \ food\ \ waste\ (g) + sewage\ \ sludge\ (\mathrm{g}) + cow\ \ manure\ (g)$$

$$Specific\ \ hydrogen\ \ yield\ = \frac{Total\ \ amount\ \ of\ \ batch\ \ hydrogen\ \ yield\ (\mathrm{mL})}{Biomass\ \ volatile\ \ solid\ \ weight\ (\mathrm{g})} \qquad (1)$$

$$Specific\ \ hydrogen\ \ conersion\ \ rate\ = \frac{Total\ \ amount\ \ of\ \ batch\ \ hydrgen\ \ yield\ (\mathrm{g})}{Biomass\ \ volatile\ \ solid\ \ hydrogen\ \ weight\ (\mathrm{g})} \times 100\% \qquad (2)$$

2.5 Statistical Analysis

Through the lag phase of solid-state fermentation hydrogen production exponential growth stage, linear regression ($y=\alpha x-\beta$) and linear fit level (R^2) values for different batches were calculated using a Microsoft Excel spreadsheet.

3.RESULTS AND DISCUSSION

3.1 Temperature effect on biogas yield, hydrogen yield, and hydrogen percentage

When biogas, hydrogen yield, and the concentration of the six temperature series were compared, they all featured a very short lag phase. For the 60℃and 70℃ series, a significant biogas and hydrogen gas high-volume wave crests occurred. No hydrogen gas was produced within the initial period. However, after 5 hours of incubation, both the biogas and hydrogen gas production rates increased, peaking after 10 hours before their respective production rates quickly declined. After 30 hours, gas production ceased, but the high hydrogen concentrations remained. The initial period was similar for the 60℃ and 50℃ series. Only during the latter part of incubation did differences appear. The 70℃ series reaction began with biogas production. Within 3 hours of incubation, it steeply dropped to zero. At 5 hours of incubation, it gradually started to create biogas and hydrogen gas. Figure 2 shows how the hydrogen gas concentration gradually dropped to around 40%.

3.2 pH effect on solid-state fermentative hydrogen yield

For the six temperature series, acidification occurred during their initial fermentation period, indicated by a rapid decrease in pH levels and a significant increase in the hydrogen yield rate. After about 10 hours of fermentation, the pH stabilized between 5.5 and 7, yielding no significant effects on the hydrogen production growth cycle of each temperature series, as shown in Figure 3.

3.3 Temperature effects on the cumulative yield comparison of hydrogen production using solid-state fermentation

After the six different batch dark anaerobic fermentation processes underwent 80 hours of incubation, their cumulative hydrogen yields were 3831, 4453, 9049, 6907, 5662, and 2533 mL. Figure 4 shows that the 60℃ series had the best cumulative output. During the exponential growth phase of each temperature series, batch linear regressions were calculated, herein, both 60 and 65 ℃ have twice exponential growth phase that can be infer to easy acidolysis component element (eg. glucose) at first stage, and the difficult acidolysis component element (eg. protein) at second stage, as shown in Figure 5. Furthermore, comparison the slope of batch hydrogen exponential growth stage yields with temperature.

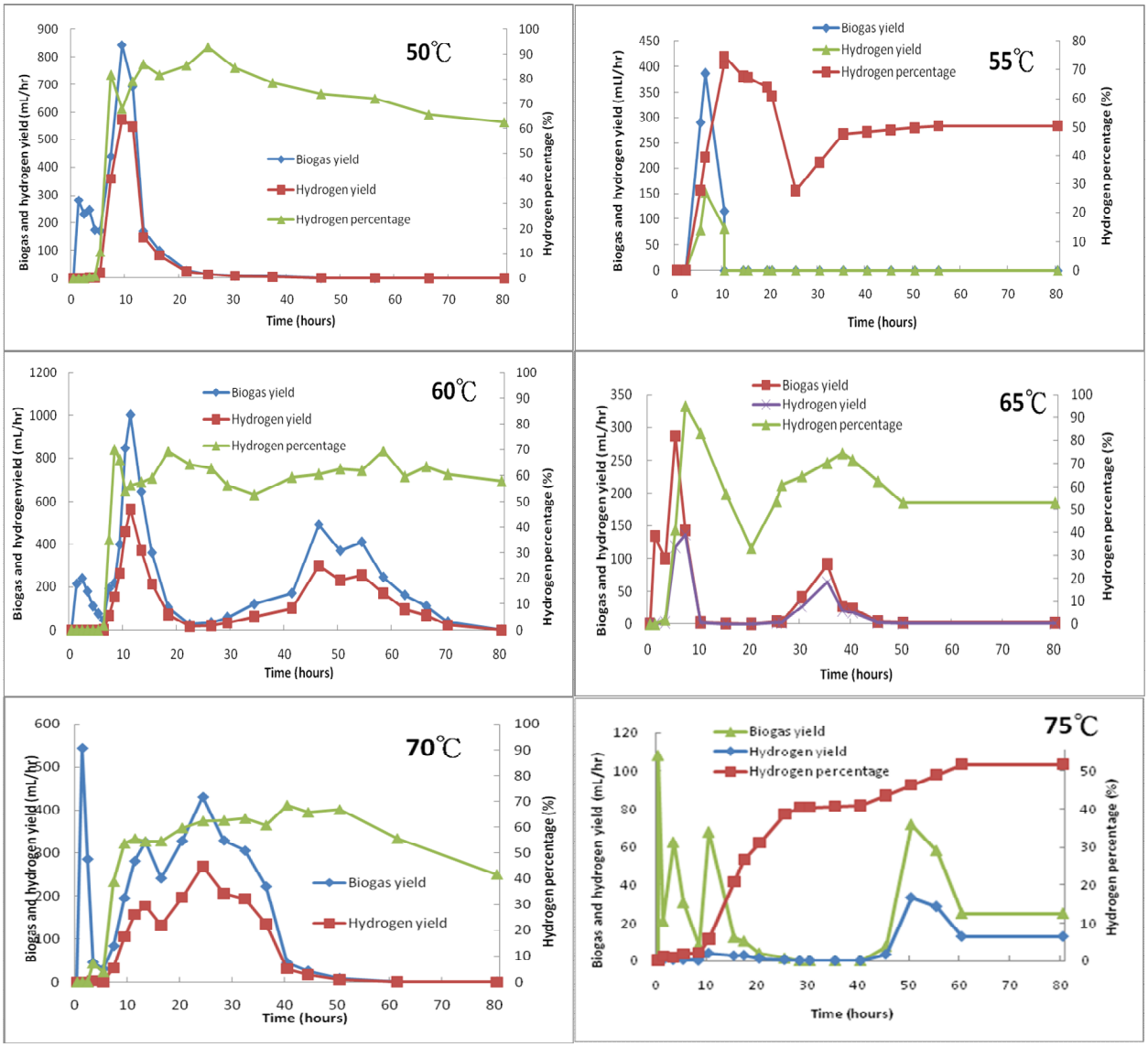

Figure 2. Temperature effect on biogas yield, hydrogen yield, and hydrogen percentage.

It can be induce to continue stirred temperature reactor (CSTR) process that have significant peak hydrogen yields in 55℃ and 65 ℃ series, as shown in Figure 6.

3.4 Temperature effects on hydrogen production efficiency using solid state batch fermentation

For six different constant temperatures, the total hydrogen yield was computed based on the ratio of hydrogen within the biogas yield. Using Equation (1) and (2), the "specific hydrogen yield" and "specific hydrogen conversion rate" were calculated. Table 2 shows the results, which demonstrated that 60 ℃ constant temperature conditions had better hydrogen production efficiency. Lastly, the hydrogen yields in this study were comparable to other hydrogen production studies, as shown in Table 3. The former published studies were conducted with glucose, xylose or starch as substrate, most of them have higher hydrogen yield than this study. However, adapting food waste and sewage sludge as mixed substrate have high specific hydrogen conversion rate.

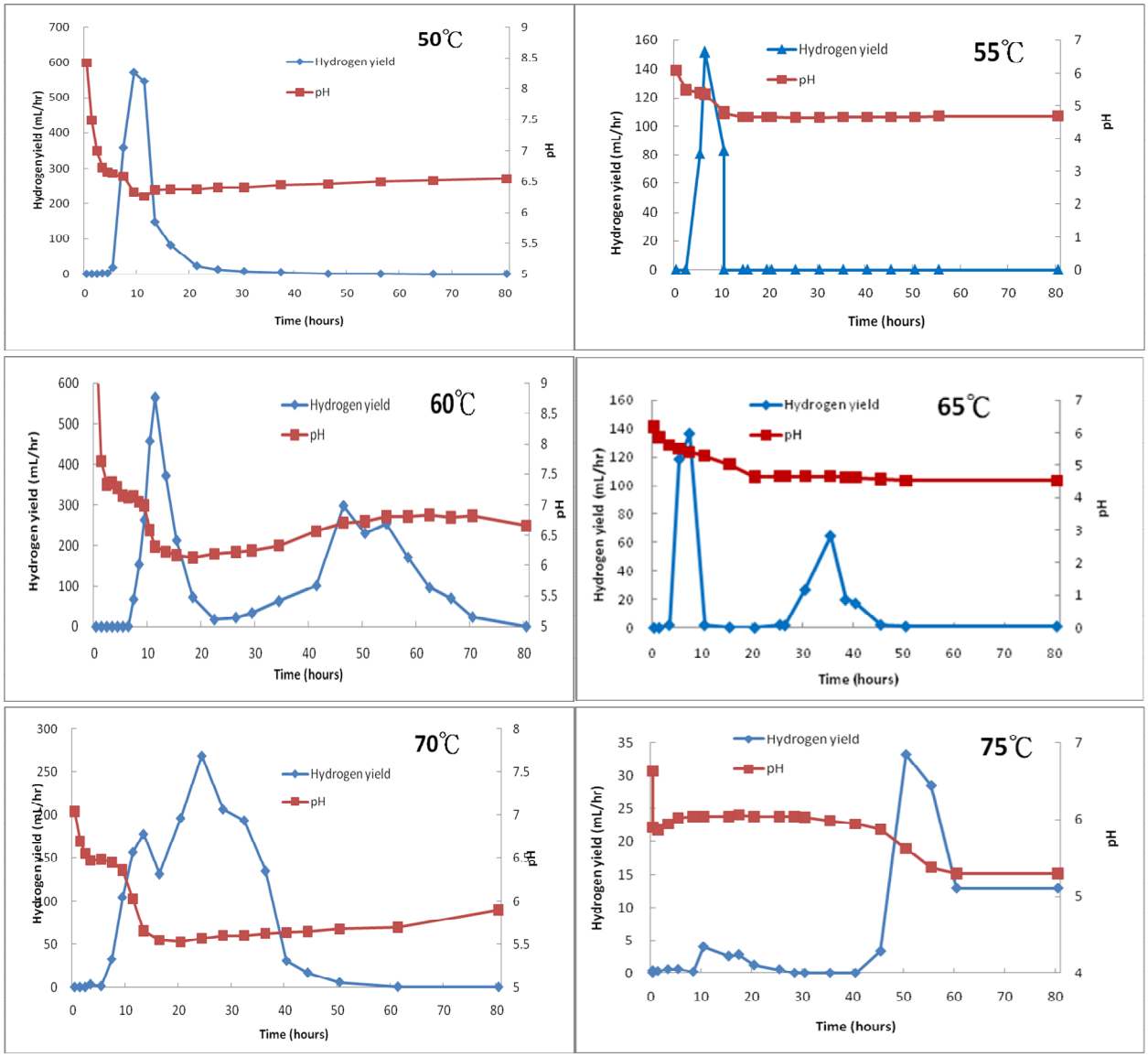

Figure 3. pH effect on solid-state fermentative hydrogen yield.

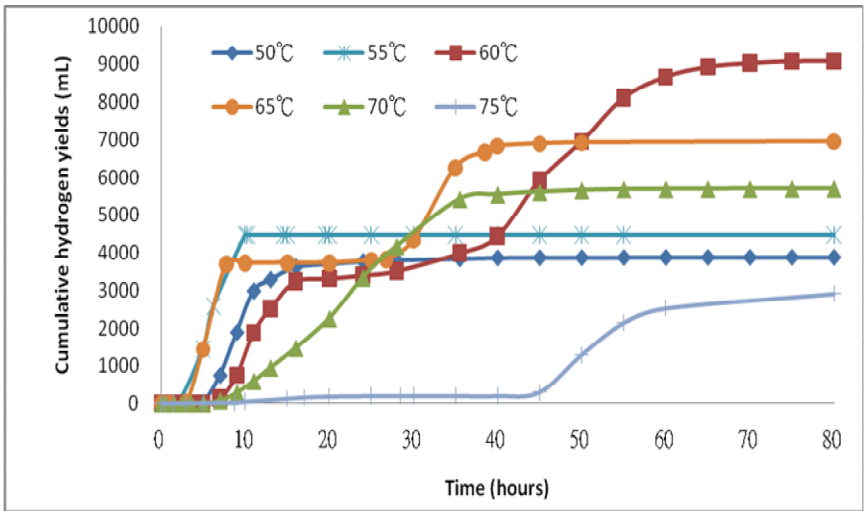

Figure 4. Temperature effects on the cumulative yield comparison of hydrogen production using solid-state Fermentation.

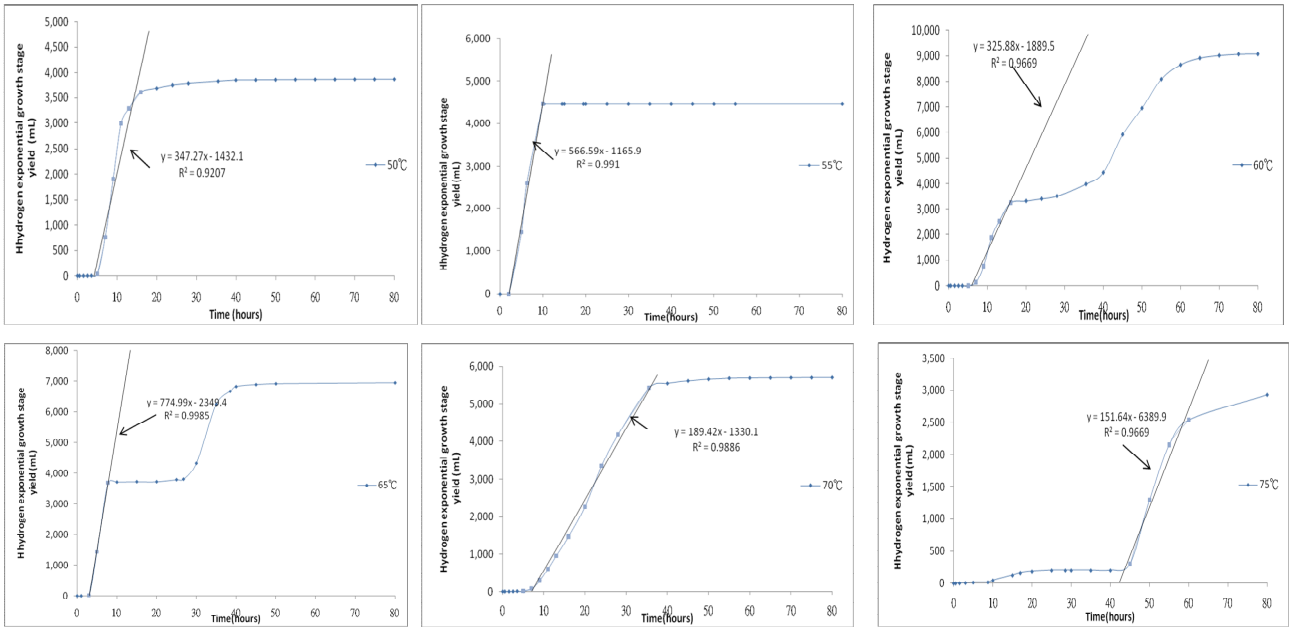

Figure 5. Regression analysis of solid-state fermentation in hydrogen exponential growth stage yield.

Table 2 - Comparison of batch solid-state fermentation hydrogen yield with temperature.

Temperature(□)	50	55	60	65	70	75
Cumulative biogas(mL)	6234	10686	15994	12457	10467	7545
Hydrogen percentage (%)	61.46	41.67	56.75	55.44	54.09	33.57
Cumulative hydrogen (mL)	3831	4453	9049	6907	5662	2533
Specific hydrogen yield ($mL\text{-}H_2/g\text{-}VS$)	16	19	39	30	24	11
Specific hydrogen conversion rate ($g\text{-}H_2/g\text{-}H$ of VS%)	1.69	1.97	4.00	3.05	2.50	1.12
Hydrogen exponential growth stage mean yield (mL/hr)	347	566	325	774	189	151

Table 3 - Comparison hydrogen yield with former published studies.

Hydrogen producing bacteria	Culture type	Substrate	Temperature examined (℃)	Optimal temperature (℃)	Hydrogen yield (mol-H_2/mol substrate)	Reference
Clostridium sp. Strain no. 2	Batch	Xylose (0.96 g-COD/L)	35	35	1.80	Taguchi et al.(1995)
Anaerobic microflora	CSTR	Glucose (0.077 g/L)	35	35	1.43	Mizuno et al.(2000)
Hydrogen-producing sludge	Batch	Glucose (7 g/L)	36	36	2.10	Fang et al.(2002)
Clostridium acetobutylicum	Batch	Glucose (2.5 g/L)	30, 33, 37, 40	37	2.00	Chin et al.(2003)
Sewage sludge microflora	CSTR	Glucose (20 g-COD/L)	15, 18, 26, 27, 30, 35	35	1.42	Lin et al.(2004)
Hydrogen-producing sludge	Batch	Glucose (10 g/L)	33, 35, 37, 39, 41	41	1.67	Chen et al.(2006)
Anaerobic sludge	CSTR, UASB	Glucose (3-7.7 g/L)	35, 55	55	1.60	Gavala et al.(2006)
Anaerobic sludge	CSTR	Glucose (0.11-0.68 g/L)	35	35	0.90	Antonopoulou et al.(2008)
Hydrogen-producing sludge	CSTR	Xylose (20 g-COD/L)	30, 35, 40, 45, 50, 55	50	1.30	Lin et al.(2008)
Digested sludge	CSTR	Starch	55	55	2.32	Akutsu et al.(2008)
CM	Batch	Food waste, sewage sludge (Glucose 22g-COD/L)	50, 55, 60, 65, 70, 75	60	1.59	This study

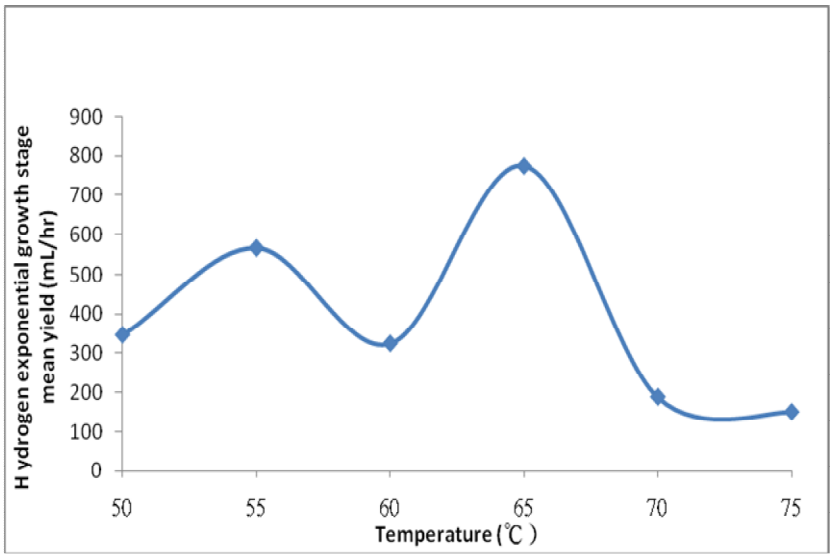

Figure 6. Comparison of hydrogen exponential growth stage yield with temperature.

5.CONCLUSIONS

Under fixed proportions of organic waste mixture with six different constant temperature fermentation series, the use of thermophilic solid-state fermentation hydrogen production with temperature as the hydrogen production bacteria screening factor, affected the hydrogen production yield.

Sewage sludge, CM, simulated non-greasy food waste, and other organic waste served as substrates. Hydrogen production characteristic of symbiotic bacteria contained in CM, in conjunction with temperature control as the screening factor, yielded a hydrogen-producing thermophilic solid-state fermentation process. This process converted hydrogen atoms into gas. The results demonstrated that this process did not need complex pre-processing of additional purchases for, or domestically cultured of, hydrogen producing bacteria. Regardless, the growth of methane bacteria was inhibited; hydrogen concentration, yield, and conversion rates also increased.

In this experiment, thermophilic solid-state fermentation completed the hydrogen production growth cycle within 80 hours. Compared to mesophilic liquid wet fermentation hydrogen production, which can last for weeks or even months based in the literature, this fermentation process has a significant control advantage.

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