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Effect of Biochar Addition and Temperature on Hydrogen Production from the First Phase of Two-Phase Anaerobic Digestion of Carbohydrates Food Waste

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ABSTRACT

This paper reports an experimental study of the effect of biochar addition and temperature on hydrogen production in the first phase of the two-phase anaerobic digestion (TPAD) of carbohydrates food waste. Anaerobic digestion experiments using white bread representing carbohydrate food wastes were conducted in bench scale 100 ml reactors. The cultures with biochar addition were placed in the reactors and incubated at different temperatures (18, 35 and 52°C) over a period of 8 days. The biochar addition ratio was varied from 0 to 18.6 g.l⁻¹. The daily volumetric hydrogen production was measured, and the cumulative yield (Y_H) and daily production rate (R_H) of hydrogen were calculated. Both biochar addition and temperature affected hydrogen production significantly. Y_H and maximum R_H increased as the biochar addition ratio increased from 0 to 10 g.l⁻¹ then decreased as the biochar addition ratio further increased up to 18.6 g.l⁻¹. At different temperatures, Y_H varied significantly, increasing from 846 ± 18 ml.l⁻¹ at 18 °C to 1475 ± 53 ml.l⁻¹ at 35°C and dropped to 1149 ± 26 ml.l⁻¹ at 52°C. The maximum R_H also peaked at 35°C, reaching 858 ± 57.1 ml.l⁻¹.day⁻¹. The effect of biochar addition was more profound under mesophilic conditions. The results of this study confirmed the beneficial effect of biochar addition in hydrogen production of carbohydrate food waste in the TPAD process.

Keywords: biogas, food waste, hydrogen, two phase anaerobic digestion

INTRODUCTION

Anaerobic digestion (AD) is one of the most mature technologies for biogas production for energy applications as well as for waste treatment [1]. Conventional AD, where a whole series of biochemical reactions take place in one reactor, produces biogas made up mainly of methane and carbon dioxide [2]. However, the reactions in conventional AD operate slowly, and the process has poor stability and is sensitive to biological and environmental changes [3]. Most importantly, being diluted by CO₂, the biogas produced has less ideal fuel properties and a low heating value if it is used in internal combustion engines [4, 5]. Two-phase anaerobic digestion (TPAD) is a subsequent anaerobic digestion which produces hydrogen in the first phase and methane in the second. When combined, the output of the TPAD is a hydrogen enriched biogas. The presence of hydrogen in the biogas would give a much improved ignition quality for gas engine applications [4, 6-9].

Biochar, a carbon rich by-product of biomass pyrolysis, has been found to promote biogas production in the conventional single phase AD owing to its ability to support biofilm formation and alleviate metabolic products inhibition [10-12]. Our previous studies also found that biochar addition in both phases of TPAD can significantly increase the production of hydrogen and methane, respectively [13]. In particular, in the first phase of TPAD, biochar supported the growth of bacteria at the beginning of the operation, allowing a shorter lag phase and production duration and preventing the cultures from severe pH drop. These led to higher yield and production rate of hydrogen compared to the cultures without biochar [13].

Temperature is a critical factor affecting hydrogen production by anaerobic digestion due to its effect on microbial growth and metabolism [14, 15]. Most anaerobic digestion operations are conducted under mesophilic (30 – 40 °C) or thermophilic conditions (50 – 60 °C) [15]. Several studies have found that thermophilic operations produced a higher hydrogen yield than mesophilic operations [16, 17] due to a higher substrate utilisation rate and suppression of hydrogen consuming bacteria. However, under thermophilic conditions, the cultures require longer time to achieve the maximum hydrogen production rate than that under mesophilic conditions. The hydrogen production under thermophilic conditions is also costly due to higher energy requirement [15], thus economically less feasible.

Our previous study examined the effect of biochar addition on hydrogen production in the first phase of TPAD at a single temperature of 35 °C. This study aimed to examine the effect of the addition of biochar on hydrogen production at different temperatures corresponding to the different operating regimes of anaerobic digestion, namely psychrophilic (18°C), mesophilic (35°C) and thermophilic (52°C). The Gompertz model was used to obtain maximum hydrogen production potentials, rates and lag phase, analysing the process of hydrogen production in this study. Practically, the results of the study offer a means of improving TPAD operation in real applications by adding appropriate biochar in the cultures and operating the process under its optimum conditions.

EXPERIMENTAL

Anaerobic digestion experiments using white bread as a representative of carbohydrate food wastes were conducted in bench scale reactors. Prior to the experimentation, the bread was shredded into ca. 1 mm. The seed sludge was a final discharge from a Wastewater Treatment Facility in Western Australia. To eliminate methanogens, the sludge was heat-treated at 95°C for 30 minutes. The presence of methanogens in the first phase of TPAD is undesirable because the methanogens converts hydrogen to methane. Biochar used in the study was the by-product of pinewood pyrolysis in an indirectly fired kiln reactor at 650°C. The results of ultimate (ASTM standards D3176) and proximate analysis (Standard Methods for the Examination of Water and Wastewater) [18] of food waste and biochar are listed in Table 1.

Figure 1 illustrates the experimental set up and procedures. The bread (8 g volatile solids.l⁻¹), heated-treated sludge (10 ml) were mixed in a 100 ml serum bottle and distilled water was added to bring the working volume to 60 ml. To set up an initial pH 6, HCl and NaOH were added. The reactor was then purged with nitrogen and sealed with a rubber stopper and a crimped aluminium lid to ensure the anaerobic condition. The reactors were incubated at 35 °C for eight days. To observe the effect of biochar on hydrogen production, biochar was added at ratios of 1.2, 5, 10, 15 and 18.6 g.l⁻¹ (w/v). A control treatment without biochar addition was also investigated. To study the effect of temperature, the cultures with the biochar addition of 10 g.l⁻¹ were incubated at different temperatures (18, 35 and 52°C). Each treatment was carried out three times.

The daily volumetric gas production was monitored using water displacement method (accuracy: ± 1 ml) [19] and then converted to volumetric biogas production under STP (273 K and 1 atm pressure). An Agilent 7980 Gas Chromatography (GC);) was used to measure gas composition. It was facilitated with flame ionisation detector (FID, accuracy: ± 50 ppm), (heater 200°C , hydrogen flow: 30 ml.min^{-1} , air flow: 350 ml.min^{-1} , make up flow: 35.5 ml.min^{-1}), back detector thermal conductivity detector (TCD) (heater 250°C , reference flow: 10 ml.min^{-1} , make up flow: 5 ml.min^{-1}) and TCD (heater 200°C , reference flow: 7 ml.min^{-1} , make up flow: 3 ml.min^{-1}) [20]. Figure 2 shows typical results of biogas composition analysis from the first phase of TPAD. The gas mainly consisted of H_2 and CO_2 . The daily hydrogen production rate (R_H) was calculated by multiplying the daily volumetric biogas by hydrogen composition in the biogas. The cumulative hydrogen yield (Y_H) was calculated by adding daily hydrogen production across the whole length of the experiment.

To determine the maximum production potential (P , unit: ml.l^{-1}), the maximum hydrogen production rate (R_{max} , unit: $\text{ml.l}^{-1}.\text{per day}$) and the lag phase (λ , unit: days), at different temperatures, the modified Gompertz [25] model was applied:

$$H(t) = P \times \exp \left\{ - \exp \left[\frac{R_{max} \times e}{P} (\lambda - t) + 1 \right] \right\} \quad (1)$$

where $H(t)$ is the cumulative hydrogen [ml.l^{-1}], and t is the time [days]. The lag phase, λ , is defined as a delayed duration required by the cultures to adapt to a new environment and start to produce hydrogen [26]. The cumulative hydrogen production results were fitted using the model.

RESULTS AND DISCUSSION

Figure 3 shows typical trends on Y_H and R_H from cultures without biochar operated at initial pH 6 and 35°C. According to Figure 3, hydrogen was produced after 12 hours and completely stopped on day 3 and produced no more gas for the remaining 5 days of the experiment. The peak of hydrogen production rate was reached on day 2, achieving 651 ml.l⁻¹.day⁻¹. The content of hydrogen in the biogas produced was up to 41%. There was no trace of methane in any cultures, suggesting that the sludge heating was effective in eliminating the methanogens. At the end of production, the cumulative hydrogen yield was 1033 ml.l⁻¹.

Figure 4 shows Y_H of cultures with additions of biochar at ratios ranging from 0 to 18.6 g.l⁻¹. After 8 days of operation, it was found that biochar addition affected hydrogen production significantly. Generally, the cultures with biochar additions produced a higher Y_H than cultures without biochar at the beginning of the incubation. The Y_H increased with increasing biochar addition ratio, with maximum Y_H of 1475 ± 53 ml.l⁻¹ observed for 10 g.l⁻¹ biochar addition ratio. This result confirms our previous findings that the biochar addition promoted the Y_H in all conditions tested. It is evident that the findings are consistent with the literature [21] and provide indirect evidence that biochar indeed acted as a microbial carrier and improved microbial activity. Biochar provides a high surface area (130.0 m².g⁻¹) for immobilising the hydrogen producing bacteria by establishing a biofilm [21]. Biochar contains 10 wt% of volatile matter that could serve as additional digestible additional nutrients [13, 22]. Furthermore, biochar

promoted higher volatile fatty acids (VFA) generation in the hydrogen production phase as reported in our previous study [13].

It is noted that the Y_H of cultures were slightly lower when the biochar addition ratio was higher than 10 g.l^{-1} . It is most likely that a biochar addition ratio higher than 10 g.l^{-1} caused an organic overload in the cultures, resulting in a shift in metabolic pathways and suppressing hydrogen production [13, 23]. Our previous study suggests that the culture with biochar addition ratio higher than 8.3 g.l^{-1} produced a high amount of propionic acid and the cultures followed the propionic pathway [24]. As a result, the hydrogen production stopped faster and generated lower Y_H than the culture incubated with 10 g.l^{-1} of biochar.

Figure 5 shows the Y_H at different temperatures in cultures incubated with biochar addition ratio of 10 g.l^{-1} . It is evident that at 35°C , the cultures started producing hydrogen earlier than cultures incubated at either 18°C or 52°C . The Y_H curve for the 35°C experiment shows that the cultures started producing hydrogen after 12 hours, with the highest yields on day 1 and 2. The Y_H then reached a plateau on day 3, suggesting hydrogen production had stopped. The Y_H curves for 52°C and 18°C shifted to the right, describing a delay before the cultures began to produce hydrogen. The 52°C and 18°C cultures reached plateau on day 7 and 9, respectively. The Y_H also varied significantly, increasing from $846.3 \pm 18 \text{ ml.l}^{-1}$ at 18°C to $1475 \pm 53 \text{ ml.l}^{-1}$ at 35°C and dropped to $1149 \pm 26 \text{ ml.l}^{-1}$ at 52°C . The maximum R_H was observed at 35°C , reaching $858 \pm 57 \text{ ml.l}^{-1}.\text{day}^{-1}$ on day 2. Overall, the cultures incubated at 18 and 52°C were less stable than at 35°C . The culture at 18°C experienced the longest lag phase of 2 days.

Before it reached the peak ($243 \text{ ml.l}^{-1}.\text{day}^{-1}$) on day 9, the R_H fluctuated. Cultures at 52°C started to produce H_2 on day 1 and reached the peak on day 6 with R_H of $265 \text{ ml.l}^{-1}.\text{day}^{-1}$. It has been reported that under both psychrophilic and thermophilic conditions, fermentative bacteria generally have slower metabolism than that under mesophilic temperature [25, 26], explaining why a maximum Y_H was observed at 35°C in this study.

To further evaluate the effect of temperature on P , $R_{\max}$ and λ with biochar addition, the experimental data in Figure 5 were fitted using Equation 1. The estimated value of each parameter generated from the fitting is summarised in Table 2. It is evident that the model could adequately describe the hydrogen production from food waste at different temperatures, with the coefficients of determination (R^2) ranging from 0.91 to 0.98 in all of the fittings. As shown in Table 2, the P was highest at 35°C ($1429 \pm 22 \text{ ml.l}^{-1}$) and lowest at 18°C ($1033 \pm 149 \text{ ml.l}^{-1}$). Similarly, $R_{\max}$ also peaked at 35°C , achieving $1000 \pm 153 \text{ ml.l}^{-1}.\text{day}^{-1}$. It is also clear that λ of the cultures incubated at 35°C was much shorter than that at other temperatures.

CONCLUSIONS

The present work has revealed that biochar addition enhances H_2 production in TPAD and revealed that the effect of biochar addition was more profound under the mesophilic conditions. Y_H increased as the biochar addition ratio increased from 0 to 10 g.l^{-1} and decreased with further increasing biochar addition ratio up to 18.6 g.l^{-1} . Y_H also varied significantly with temperature and a maximum Y_H of $1475 \pm 53 \text{ ml.l}^{-1}$ was observed at 35°C , minimum Y_H of $846 \pm 18 \text{ ml.l}^{-1}$ at 18°C . and at 52°C , Y_H was 1149 ± 26

208 ml.l⁻¹. The results of the Gompertz model analysis suggest that R_{max} also peaked at 35°C,
209 reaching 1000 ± 153 ml.l⁻¹.day⁻¹, with the highest P (1426 ± 22 ml.l⁻¹) and the shortest lag
210 phase of 0.5 ± 0.09 day.

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221 **NOMENCLATURE**

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TPAD	two phase anaerobic digestion
Y_H	hydrogen yield
R_H	hydrogen production rate
AD	anaerobic digestion
ASTM	American society of testing and materials
EPA	environmental protection agency
g	Gram
ml	milliliter
l	Liter
HCl	hydrochloric acid
NaOH	Sodium hydroxide
w/v	weight per volume
STP	standard temperature and pressure
GC	gas chromatography
FID	flame ionisation detector
TCD	thermal conductivity detector
$H(t)$	cumulative hydrogen production

P	maximum hydrogen production potential
R_{max}	maximum hydrogen production rate
e	natural number
λ	lag phase
t	Time
C	Carbon
N	Nitrogen
H	Hydrogen
S	Sulfur
O	Oxygen
C/N	carbon to nitrogen ratio
TS	total solids
VS	volatile solids
ARC	Australia Research Council

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Figure Captions List

- Fig. 1 A schematic showing the experimental set up (a) anaerobic digestion
 experimental procedure (b)
- Fig. 2 A typical gas chromatogram of gas collected from the first phase of TPAD
- Fig. 3 Cumulative yields and production rates of hydrogen production from
 food waste without biochar operated at initial pH 6 and 35 °C
- Fig. 4 Cumulative hydrogen yields (Y_H) at different biochar addition ratios of
 cultures operated at initial pH 6 and 35 °C
- Fig. 5 Cumulative hydrogen yields and production rate at different
 temperature at 10 g.l⁻¹ of biochar addition

Figure 1

Figure 1 A schematic showing the experimental set up (a) and anaerobic digestion experimental procedure (b)

Figure 2

Figure 2 A typical gas chromatogram of gas collected from the first phase of TPAD

Figure 3

Figure 3 Cumulative yields and production rates of hydrogen production from food waste without biochar operated at initial pH 6 and 35 °C

Figure 4

Figure 4 Cumulative hydrogen yields (Y_H) at different biochar addition ratios of cultures operated at initial pH 6 and 35 °C

Figure 5

Figure 5 Cumulative hydrogen yields and production rate at different temperature at 10 g.l⁻¹ of biochar addition

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Table Caption List

Table 1	The results of ultimate and proximate analyses of the food waste and biochar
Table 2	The results of calculation using modified Gompertz fitting equation on hydrogen production with 10 g.l ⁻¹ biochar addition at 18, 35 and 52°C

*) N.D: not determined

Table 2 The results of calculation using modified Gompertz fitting equation on
hydrogen production with 10 g.l⁻¹ biochar addition at 18, 35 and 52°C

Temperature (°C)	P (ml.l ⁻¹)	R _{max} (ml.l ⁻¹ .day ⁻¹)	λ (day)	R ²
18	1033±149	122±19	2.7±0.5	0.91
35	1429±22	1000±153	0.5±0.09	0.95
52	1175±23	300±26	2.4±0.17	0.98