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EFFECT OF TEMPERATURE AND TOTAL SOLIDS CONCENTRATION ON HYDROGEN PRODUCTION FROM RICE WASTE

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ABSTRACT

A study was conducted to ascertain the effect of temperature and total solids (TS) on the hydrogen production potential of rice waste. This study used sludge as the source of Clostridium in equal proportion with rice waste on total solid basis. At 37°C the hydrogen yield was 26.39 mL/g-VS_{fed}, 58.4mL/g-VS_{fed} and 2.95 mL/g-VS_{fed} in 5%, 10% and 15% TS reactors, respectively, whereas at 55°C the hydrogen yield was 8.19 mL/g-VS_{fed}, only in 10% TS reactor. However, in 5% and 15% TS reactors, the hydrogen production was negligible. In all reactors, the maximum hydrogen yield was produced during 24 to 72 hours of incubation. The production of volatile fatty acids increased with time in all reactors at both temperatures (37°C and 55°C). For an economical generation of hydrogen from co-digestion of sludge and rice waste, the mix culture of Clostridium obtained from sludge at 37°C would be the best choice when used in equal proportion with rice at 10% TS.

Keywords: Clostridium, hydrogen yield, initial total solids, rice waste temperatures.

INTRODUCTION

Hydrogen is an alternate source of energy with a total energy content of 122kJ/g. It is pollution free because hydrogen produces water during combustion. Therefore, hydrogen may be used in the replacement of fossil fuels (Pisutpaisal *et al*., 2012). Hydrogen can be produced by two methods namely biological and non-biological (Chen *et al*., 2006). Biological methods include Photo-fermentation and dark fermentation. Photo fermentation method uses sunlight through

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photosynthetic and chemosynthetic-fermentative bacteria (Antonopoulou *et al*., 2010). Dark fermentation uses Clostridia and Enterobacteria that produce high yields of hydrogen and is more popular than photo fermentation (Xie *et al*., 2010). In dark fermentation method, sludge (64 to 70% Clostridium) is commonly used for hydrogen production under mesophilic as well as thermophilic temperature conditions (Li and Liu, 2012; Saripan and Reungsang, 2014) due to its low cost and high availability. Non-biological methods include Electrochemical or Thermochemical processes that consume high energy to produce hydrogen and are not environmental friendly (Kapdan *et al*., 2006). Food waste is a widely tested material for hydrogen production (Fountoulakis *et al*., 2009). In China, rice waste (RW) has a share of 10 to 15 % in food waste produced at hotels (Shiwei, 2005). The RW is carbohydrate rich waste that makes it a suitable for hydrogen generation (Fang *et al.,* 2006). Moreover a little information is currently available on RW that is not enough to provide clear guidelines about hydrogen generation from it (Dong *et al*., 2009). The sludge contains hydrogen consumers that can reduce the yield, so pre-treatment is required to inactivate them. The most suitable and widely opted pre-treatment is a heat treatment of seed sludge (Oh *et al*., 2003) which is done at different temperatures and time (Li and Fang, 2007). However, previous studies have reported a specific initial quantity of waste for hydrogen production or carbohydrate contents of waste as reactor start up (Fang *et al*., 2006; Dong *et al*., 2009), which does not provide satisfactory hydrogen production under various mesophilic and thermophilic temperatures. Therefore this study was carried out to find out the impact of temperatures (37°C and 55°C) and total solids (TS) concentration on hydrogen production from sludge and rice waste.

MATERIALS AND METHODS

Seed sludge

The study was conducted at Agricultural Material Characteristics Research Laboratory, College of Engineering, Nanjing Agricultural University, Nanjing, China. The sludge was collected from a wastewater settling channel of Pokou, Nanjing, it was washed and sieved to remove unwanted materials (Nathao *et al*., 2013). Later, the sludge was placed in preheated oven at 100˚C for 15 minutes to deactivate methanogens (Li and Fang, 2007).

Rice waste

Food waste mainly consisted of rice, meat and vegetables was collected from the canteen at Engineering College, Nanjing Agricultural University, Nanjing, China. Rice waste was manually separated from food waste and ground in food grinder by adding water at 1:1 to make rice slurry (Reungsang *et al*., 2013).

Experimental set-up

Lab scale reactors with 550 mL capacity and working volume of 400 mL were used in this study. These reactors were connected to a hydrogen collection system and avacuum was created in the head space to maintain anaerobic conditions. These reactors were placed into a water bath equipped with thermostatically controlled heater. In order to provide proper mixing, reactors were shaken manually many times a day 3% NaOH solution was added in gas collecting bottles to remove CO_2, NH_3 and H_2O. The volume of the NaOH displaced from the bottle was equivalent to volume of hydrogen produced that was measured by a measuring cylinder connected to gas collecting bottles (Fang *et al*., 2006; Saraphirom *et al*., 2010; Lin *et al.*, 2013). Samples collected before and during the experiment were stored in the refrigerator (0-4°C).

Batch experiments of hydrogen production

In order to study the impact of initial TS on hydrogen production, three reactors were used with rice waste to seed sludge (1:1) (Zhu *et al.,* 2008). The initial TS concentration was kept at 5%, 10% and 15%. First of all, these reactors were placed at 37 ±0.1°C in water at second set of experiments; these reactors were placed at 55 ±0.1°C in the water bath. Initial pH of all reactors was maintained at 7. All the experiments were arranged in a Completely Randomized Design (CRD) with three replications.

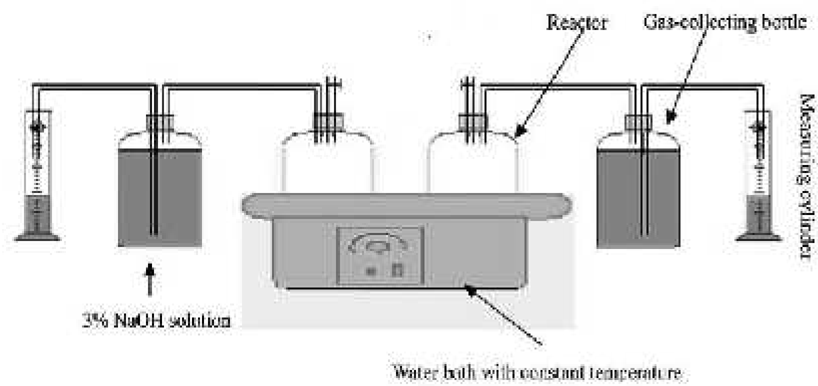

Figure 1. Experimental Layout.

Analytic methods

The volume of hydrogen was measured by the liquid displacement method using 3% NaOH solution. Total solids were measured by oven dried method at 105°C and volatile solids (VS) were measured by furnace method at 550°C. The chemical oxygen demand (COD) was measured by open reflux method. The alkalinity and volatile fatty acids were measured by 0.01M NaOH and 0.01M H_2SO_4 using standard procedures (APHA, 2005).

Kinetic modeling

The cumulative hydrogen production in the batch experiments, followed the modified Gompertz equation (Dong *et al.*, 2009).

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

Where

H= cumulative hydrogen production (mL)
t= time (h)
P = hydrogen production potential (mL)
R_m = maximum hydrogen production rate (mL/h)
λ = lag phase duration (h)
e= exponential 2.718

These values were estimated in Matlab (2010a) using curve fitting option. The maximum specific hydrogen production rate (L/(g-VS d)) was calculated by dividing R_m with initial VS in the reactor. The hydrogen yield (mL/g-glucose) was calculated by dividing P with glucose content of reactor (Liu *et al*., 2013).

RESULTS AND DISCUSSION

Hydrogen production

The cumulative hydrogen production under mesophilic temperature (37°C) is shown in Figure 2. At 37°C the hydrogen yield was 26.39 mL/g-VS_{fed}, 58.4mL/ g-VS_{fed} and 2.95 mL/g-VS_{fed} in 5%, 10% and 15% TS reactors, respectively, whereas at 55°C the hydrogen yield was 8.19 mL/g-$VS_{fed,}$ only in 10% TS reactor. However, in 5% and 15% TS reactors, the hydrogen production was negligible. Gas production began shortly after incubation in 5% TS reactor at 37°C, whereas gas production was started after 12 and 24 hours in 10 % and 15% TS reactor, respectively. This is attributable to Liu *et al*. (2013), who found maximum hydrogen production during 24 to 60 hours of incubation in all reactors at 37°C. It represented a direct relationship between gas production time and TS concentration at 37°C. However, production in 5% and 15% TS reactors at 55 ^oC may be attributable to the wastes having higher content of carbohydrates (Fang *et al*., 2006). After 72 hours, hydrogen production dropped to zero in all reactors. That might be due to the initial deactivation of hydrogen consumers (homoacetogens such as methanegenic) by thermal treatment (Oh *et al*., 2003). Hydrogen yield estimated on carbohydrate (glucose) basis was the highest at 10 % TS under mesophilic conditions. The highest yield obtained in this study was the smaller than 346 mL/g-carbohydrate as reported by Fang *et al.* (2006), because they used pH control. However, in our study pH control was not taken into account provided.

The maximum yield of 208.5 mL/g-COD was obtained in 10% TS reactor, which was much higher than that achieved for food waste (Chen *et al*., 2006). Somewhat similar results were also achieved by Twakif and Qelish (2014). This increase in yield also showed better removal of organic matter content during rice waste digestion as compared to food waste.

Table 1. Kinetic parameters and hydrogen yield.

TS (%)	P (mL)		R_m (mL/h)		λ (h)		(mL/g-VS $_{fed}$)		Hydrogen yield (mL/g glucose)		(mL/g COD)	
	37°C	55°C	37°C	55°C	37°C	55°C	37°C	55°C	37°C	55°C	37°C	55°C
5	204.5	-	4.77	-	3.68	-	26.39	-	181.81	-	116.85	-
10	876	122.9	23.62	4.29	31.3	35.02	58.4	8.19	204.6	65.57	208.57	29.26
15	65	-	30.47	-	25.3	-	2.95	-	130.08	-	30.95	-

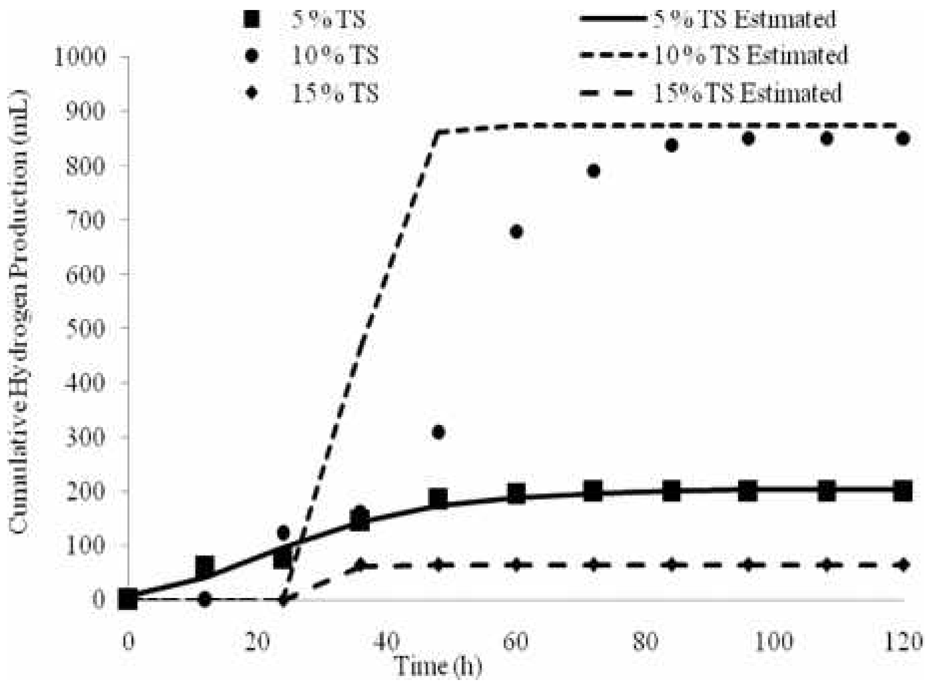

Figure 2. Cumulative hydrogen production at 37 °C

Fermentation process stability

Stability of anaerobic process can be measured in term of VFA, alkalinity and pH. The reduction of free fatty acids with time caused reduction in pH, the buffering capacity of the reactor. The Figure 4, shows that the final pH of all reactors was more than 4 except 10% TS reactor under mesophilic conditions. However, the final pH of 10% thermophilic reactor and 10% mesophilic reactor was 0.5, which is close to the findings of Gadow *et al*. (2012). Only 10 % TS represented higher pH than other reactors under thermophilic conditions as it stopped producing hydrogen early as compared to the reactor under mesophilic conditions.

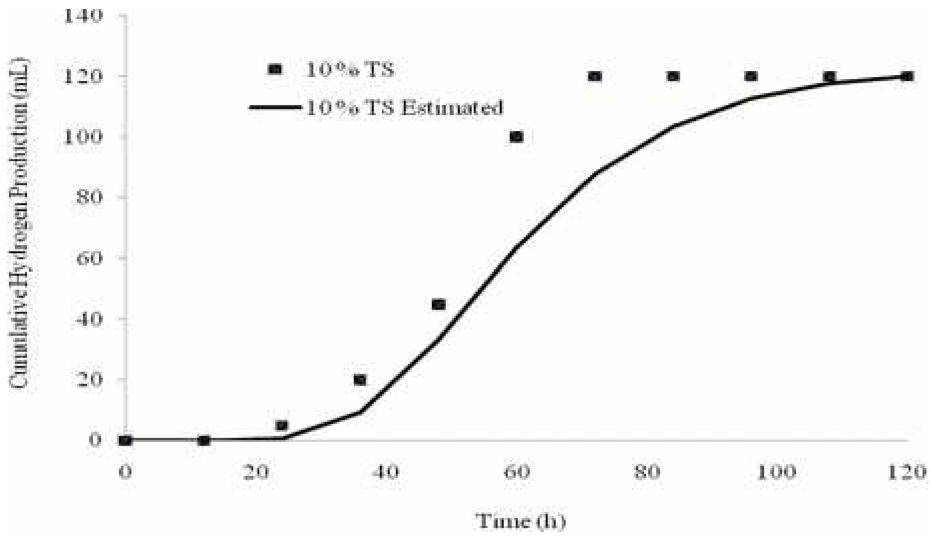

Figure 3. Cumulative Hydrogen production at 55 °C

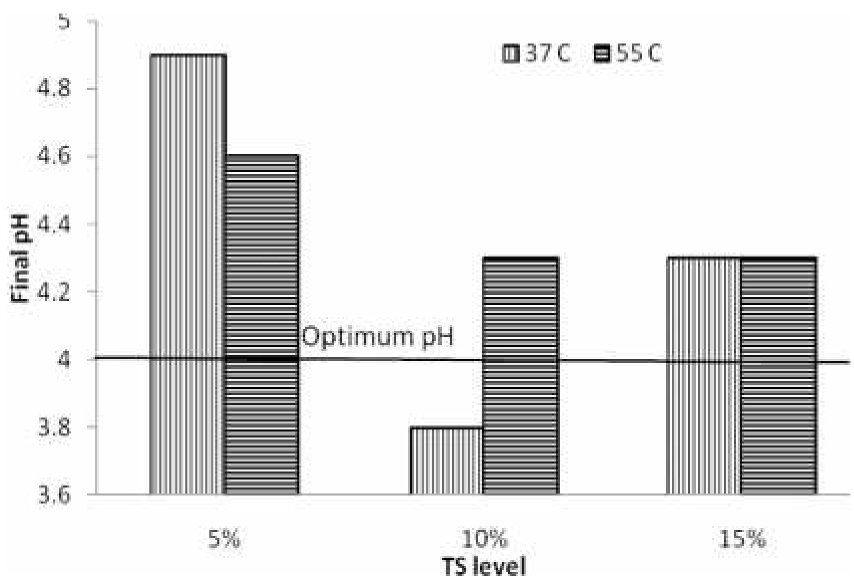

Figure 4. The pH at the end of incubation

Alkalinity is considered as another process stability parameter along with pH. For a better fermentation process, the alkalinity should be below 5000 mg/L (Ren *et al*., 2004). In this study alkalinity remained less than 5000 mg/L, while the drop of alkalinity was observed at the end of incubation time as shown in Figure 5. The maximum drop in alkalinity was observed in 10% TS reactor under mesophilic conditions due to the lowest final pH as compared to other reactors. Alkalinity in thermophilic reactors remained smaller than that observed in mesophilic reactors except for 5 % TS reactor where thermophilc alkalinity was higher than mesophilic alkalinity. This change in alkalinity was also reported by Lin *et al.* (2013).

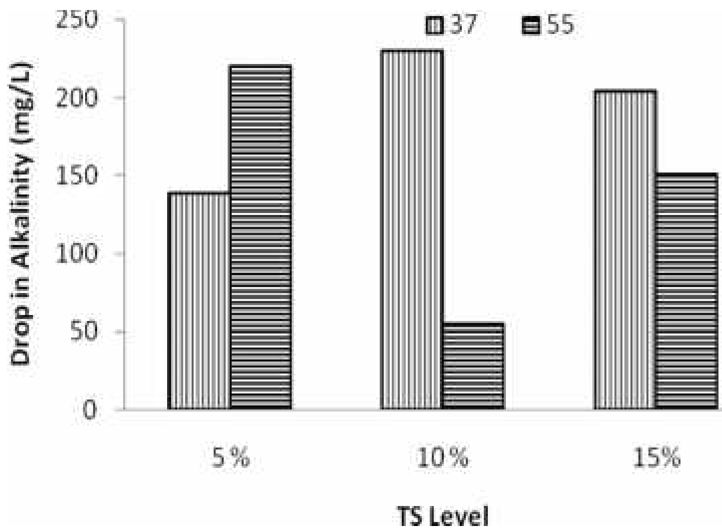

Figure 5. Alkalinity drop under different treatments

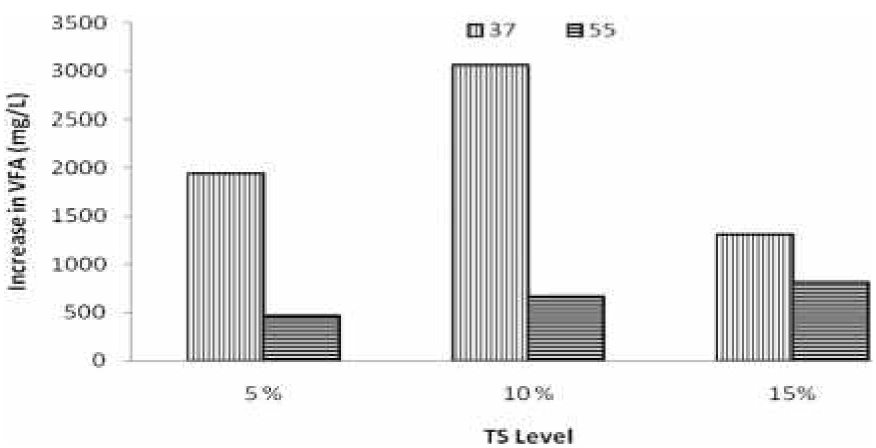

Figure 6. The VFA increase under different treatments

The VFA represented biodegradable organics in the reactor. Its higher concentration led to drop in pH. The 10% had lowest pH at the end of the process (Figure 3) and these two reactors experienced a maximum increase in VFA (Figure 6). It was also observed that VFA increased with time and the mesophilic process had higher VFA compared to thermophilic as reported by Lin *et al*. (2013). The increase in VFA also represented the efficient microbial activity (Figure 6). The increase in temperature from mesophilic to thermophilic also lowered the hydrogen production at thermophilic temperature, which might be due to the growth of *Clostridium aceticum* (Sim *et al.*, 2007).

CONCLUSION

This study has shown that the maximum hydrogen yield was obtained at 37°C in 10% TS reactor compared to 5 and 15%. However, at 55°C the hydrogen yield was observed only in 10% TS reactor, while in 5 and 15% TS reactors, the hydrogen production was negligible. At both temperatures, the optimal incubation time for production of hydrogen was found 24 to 72 hours. Therefore, cheap and effective hydrogen production is from co-digestion of sludge and rice waste. The best source of Clostridium may be obtained at 37 ^{0}C during 24 to 72 hours.

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