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Effect of COD Loading Rate on Hydrogen Production from Alcohol Wastewater

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***Abstract*—**The objective of this study was to investigate hydrogen production from alcohol wastewater by anaerobic sequencing batch reactor (ASBR) under thermophillic operation. The ASBR unit used in this study had a liquid holding volume of 4 L and was operated at 6 cycles per day. The seed sludge taken from an upflow anaerobic sludge blanket unit treating the same wastewater was boiled at 95 °C for 15 min before being fed to the ASBR unit. The ASBR system was operated at different COD loading rates at a thermophillic temperature (55 °C), and controlled pH of 5.5. When the system was operated under optimum conditions (providing maximum hydrogen production performance) at a feed COD of 60 000 mg/l, and a COD loading rate of 68 kg/m^3 d, the produced gas contained 43 % H_2 content in the produced gas. Moreover, the hydrogen yield and the specific hydrogen production rate (SHPR) were 130 ml H_2/g COD removed and 2100 ml H_2/l d, respectively.

***Keywords*—**Biohydrogen, Alcohol wastewater, Anaerobic sequencing batch reactor (ASBR), Thermophillic operation

I. Introduction

IT is a fact that energy is a necessity in daily life. The shortage of energy seems to occur in the near future due to an increasing consumption. Therefore, renewable energy is considered to be an alternative to reduce the demand of fossil fuels. Among alternative fuels, hydrogen is the most interesting one because it is a clean fuel (water is produced in the combustion process and does not produce carbon dioxide) and also gives high-energy yield. Hence, hydrogen has been suggested as a future fuel [1]. In addition, hydrogen can be used to generate electricity through fuel cells [2].

Hydrogen can be produced in several ways: steam reforming of natural gas, thermal cracking of natural gas, pyrolysis or gasification of biomass, and electrolysis of water. All of them require high energy to operate. Moreover, they are not environmentally friendly [3]-[6] and risky in operation. A better way used to produce hydrogen is biological hydrogen production processes because they can be operated under ambient condition [1]. The biological hydrogen production processes can be classified into 2 types: photo and dark fermentations. The dark fermentation is more favorable due to its constant production of hydrogen without light. Various raw materials have been widely used as a substrate in hydrogen production for example, cassava wastewater [7], food waste [8], starch wastewater [9], wheat powder solution [10], and industrial wastes [11].

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Sreethawong *et al.,* [7] studied hydrogen production from cassava wastewater; gaining a maximum hydrogen production in terms of specific hydrogen production rate (SHPR) at 388 ml H_2/g VSS d. Sik Shin *et al.,* [8] reported the hydrogen production from food waste under thermophillic condition was higher than that under mesophillic condition. Lee *et al.,* [12] showed the pH-dependency for hydrogen production from cassava starch. The suitable pH range of pH 5.5 to 6.0 displayed better hydrogen production performances; as it gave better environment for the cells to utilize starch for growth.

In this present work, alcohol wastewater was used to produce hydrogen using anaerobic sequencing batch reactor (ASBR) under thermophillic operation.

II. Experimental

A. Seed sludge preparation

The seed sludge obtained from the biogas plant of Sapthip Lopburi Co., Ltd., Thailand was first concentrated by sedimentation, and the concentrated sludge was ground and filtered through a 1 mm sieve to remove debris and large sand particles. After that, it was boiled at 95 °C for 15 min in order to enrichhydrogen-producing acidogenic bacteria and to eliminate hydrogen-consuming methanogens [10],[13]-[17]. The heat-treated sludge was then added to the studied anaerobic sequencing batch reactor (ASBR).

B. Studied wastewater

The alcohol wastewater was also obtained from the same factory which cassava is used as a raw material for alcohol fermentation. Table 1 shows the characteristics of the studied alcohol wastewater. It was filtered through a 0.2 μm sieve to remove any large solid particles before use. The alcohol wastewater had a chemical oxygen demand (COD) value of about 60000 mg/l and the ratios of COD: nitrogen: phosphorous of 100:2:0.4, indicating that both element were sufficient for anaerobic degradation (the theoretical ratio of COD:N:P = 100:1:0.4 for anaerobic decomposition). Therefore, an addition of nutrients was not required in this study.

C. ASBR operation

Two identical units of anaerobic sequencing batch reactors (ASBR) were used independently to perform the hydrogen production at different COD loading rates. The bioreactors were operated with a working volume of 4 liters. The schematic of the studied ASBR system is shown in Figure 1. The ASBR operation consisted of 4 steps: feeding, reacting, settling, and decanting. The time of each step was controlled by timers. First, for the feed step, the alcohol wastewater was introduced into the top of the reactor.

A heater (equipped with thermocouple) and a pH-controller (with 1 M NaOH) were used to maintain a constant temperature and solution pH in the studied ASBR. Hwang et al., [18] found that the maximum biogas production was observed at pH 5.5 and a higher pH resulted in lowering hydrogen production. Moreover, Lee et al., [12] also reported that the system operated at pH 5.5 gave the highest the hydrogen production. Hence, in this work, the studied ASBR reactors were operated at a solution pH of 5.5. For procedure quantity of 1000 ml of the heat-treated sludge was added to each of the studied ASBR reactor. In this present work, the ASBR operation times of four sequential steps at 6 cycles per day are shown in Table 2. The 6 cycles per day was used to operate the studied ASBRs because it was proven in previous work to give the highest hydrogen production performance [7]. Table 3 shows the flow rate of either feed or decant at different COD loading rates and a constant temperature of 55 °C. At any given COD loading rate, the studied ASBR reactor was operated around two weeks to reach the steady state before being taken effluent samples and produced gas for analysis and measurement. Steady state conditions were attained when both effluent BOD and gas production rate were invariant with time.

D. Measurements and analytical methods

The gas production rate was measured by using a wet gas meter. The amount of gas composition in produced gas was analyzed by a gas chromatograph (AutoSystem GC, Arnel PerkinElmer) equipped with a thermal conductivity detector (TCD) and a stainless-steel HayeSep D 100/120 mesh packed column (Alltech). The total amount of volatile fatty acids (VFA) in the effluent samples was determined by the distillation and titration method [19]. The VFA composition in the effluent samples was analyzed by another gas chromatograph (PR2100, Perichrom) equipped with a flame ionization detector and a DB-WAXetr capillary column (J & W Scientific). The mixed liquor volatile suspended solids (MLVSS) in the effluent samples taken during the reacting step to represent the microbial concentration and volatile suspended solids (VSS) in the effluent samples taken during the decanting step to represent the microbial washout from the system were measured according to the standard methods [19]. The COD in the feed and effluent samples was determined by the dichromate method using a COD analyzer (DR 2700, HACH). The average values of the analysis results (with less than 5% standard deviation) were used to access the process performance of the studied ASBR system.

TABLE I
CHARACTERISTICS OF THE STUDIED ALCOHOL WASTEWATER

Parameter	Unit	Value
pH	-	3.4
COD	mg/l	60 000
Total solids (TS)	mg/l	10 000
Total phosphorous	mg/l	800
Total nitrogen	mg/l	4000
Ammonia (NH_3)	mg/l	70
Nitrate (NO_3)	mg/l	400
Nitrite (NO_2)	mg/l	2
COD:N:P	-	100:2:0.4
Color	-	Blown

TABLE II
OPERATION CONDITION FOR FOUR SEQUENTIAL STEPS OF STUDIED ASBR PROCESS AT 6 CYCLES PER DAY

Operating step	Cyclic time (min)
Feed	15
React	90
Settle	120
Decant	15
Total	240

TABLE III
OPERATION CONDITION FOR THE STUDIED ASBR PROCESS AT DIFFERENT COD LOADING RATES

Feed and Decant (l/d)	HRT (h)	Feed and Decant (l/cycle)	COD loading rate (kg/m^{3}d)
3.00	32	0.500	45
3.75	25.6	0.625	56
4.50	21.3	0.750	68
5.25	18.3	0.875	79

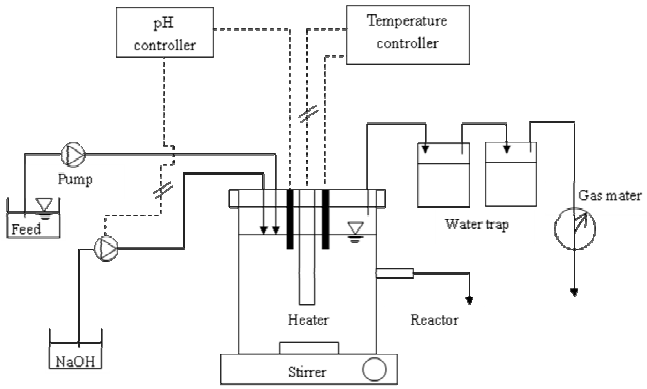


Fig. 1 Schematic of studied ASBR process

III. RESULT AND DISCUSSION

A. Organic removal results

The effect of COD loading rate on COD removal efficiency and gas production rate is shown in Figure 2a. The COD removal efficiency increased with increasing COD loading rate from 45 to 68 kg/m^{3}d and then decreased with further increasing COD loading rate. The maximum COD removal efficiency was 32 % at a COD loading rate of 68 kg/m^{3}d. The increase in COD loading rate results in an increase in organic compounds available for microbial degradation, leading to

increasing COD removal. However, at a very high COD loading rate greater than 68 kg/m^{3}d, the system started having too high VFA, causing increasing toxicity to the microbes and then lowering the COD removal which will be further discussed later.

Figure 2b shows the gas composition in the produced gas and hydrogen production rate at different COD loading rates. Under the studied conditions, the produced gas contained mainly hydrogen and carbon dioxide without methane, suggesting that the methanogenic step was completely suppressed which is in a good agreement with previous results [20]-[21].The hydrogen percentage increased with increasing COD loading rate and reached a maximum of 43% at a COD loading rate of 68 kg/m^{3}d. After that it decreased with further increasing COD loading rate from 68 to 79 kg/m^{3}d. The same explanation used for the effect of COD loading rate on the COD removal can be applied for that on the gas production rate, and hydrogen percentage in the produced gas [7],[10],[20],[22] which will be further discussed later. For carbon dioxide percentage, it has an opposite trend to the hydrogen percentage.

B. Hydrogen production results

The hydrogen production rate as a function of COD loading rate is shown in Figure 2b which is calculated from the gas production rate and gas composition. Similar to the gas production rate, the hydrogen production rate increased with increasing COD loading rate and reached a maximum at a COD loading rate of 68 kg/m^{3}d. It decreased with further increasing COD loading rate beyond 68 kg/m^{3}d. As mentioned before, the increase in hydrogen production rate with increasing COD loading rate because of the increase in organic compounds in the system available for microbes which can convert organic compound to hydrogen gas. At a high COD loading rate, especially 79 kg/m^{3}d the hydrogen production rate decreased because of the toxicity from VFA accumulation.

The specific hydrogen production rate (SHPR) is calculated from hydrogen production rate per liquid working volume or microbial concentration. The SHPR as a function of COD loading rate is shown in Figure 2c. The SHPR increased with increasing COD loading rate and attained a maximum value of 525 ml H_2/g MLVSS d (or 2100 ml H_2/l d) at a COD loading rate of 68 kg/m^{3}d which correspond to the maximum hydrogen production and hydrogen percentage at this COD loading rate. Moreover, the SHPR decreased to 185 ml H_2/g MLVSS d (or 570 ml H_2/l d) with further increasing COD loading rate to 79 kg/m^{3}d, corresponding to a decrease in the hydrogen production rate.

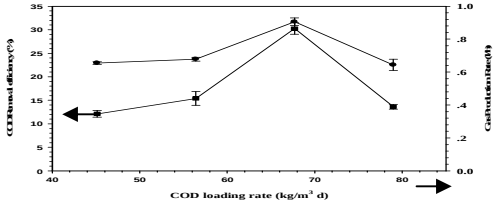
The hydrogen yield is calculated from a hydrogen production rate per g of COD applied or COD removed. The effect of COD loading rate on both hydrogen yields is shown in Figure 2d. The hydrogen yield increased with increasing COD loading rate and attained a maximum value of 130 ml H_2/g COD removed or 85 ml H_2/g COD applied at a COD loading rate of 68 kg/m^{3}d. Afterwards, it decreased markedly to 31 ml H_2/g COD removed or 5 ml H_2/g COD applied with further increasing COD loading rate to 79 kg/m^{3}d. At the highest hydrogen yield was found to correspond to the highest ability of microorganisms to convert organic compounds to hydrogen gas. Regarding the hydrogen production performance in term of hydrogen production rate, SHPR, and hydrogen yield, a COD loading rate of 68 kg/m^{3}d is considered to be an optimum condition.

C. Volatile fatty acid (VFA) results

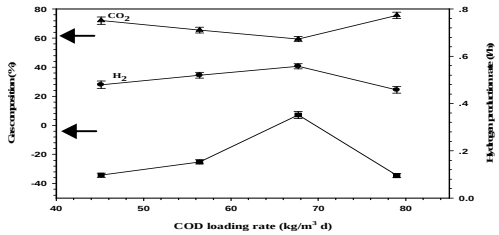
Figure 3 shows the effect of COD loading rate on the total VFA concentration (mg/l as acetic acid) in the ASBR system. The total VFA increased with increasing COD loading rate. The highest total VFA concentration of 10400 mg/l as acetic acid was found at a COD loading rate of 79 kg/m^{3}d which was responsible for both reductions of COD removal and hydrogen production efficiency, as describe before. From the results, it can be concluded that a maximum VFA for hydrogen production from this alcohol wastewater is around 9000 mg/l as acetic acid. A slight increase in VFA from 9000 mg/l to 10 400 mg/l exhibited significant toxicity to the microbial activity toward hydrogen production production performance.

The effect of COD loading rate on VFA composition and ethanol concentration in the bioreactor is also shown in Figure 3. The main components of VFA were acetic acid, propionic acid, butyric acid, and valeric acid. Both acetic and propionic acids increased slightly with increasing COD loading rate throughout the studied range of COD loading rate. However butyric and valeric acids increased substantially when the COD loading rate increased from 68 kg/m^{3}d to 79 kg/m^{3}d. . At any given COD loading rate, butyric acid was the highest and followed by valeric acid, acetic acid and propionic acid. As known, a high amount of butyric acid or acetic acid concentration can lead to a higher hydrogen production performance. In contrast, a higher amount of propionic acid can result in lowering higher hydrogen production performance. To maximize the hydrogen production performance, an anaerobic system should be operated to have high butyric acid and acetic acid concentration with a very low propionic concentrations [23] -[25].O-thong *et al.*, [26] also found that high amounts of butyric acid (6200 mg/l), and acetic acid (4300 mg/l) with a low amount of propionic acid (120 mg/l) contributed to the highest hydrogen production from palm oil wastewater. The butyric acid and acetic acid are formed via the metabolic pathway for the production of hydrogen [27]. The propionic acid concentration is formed via the metabolic pathway for the consumption of hydrogen [27].

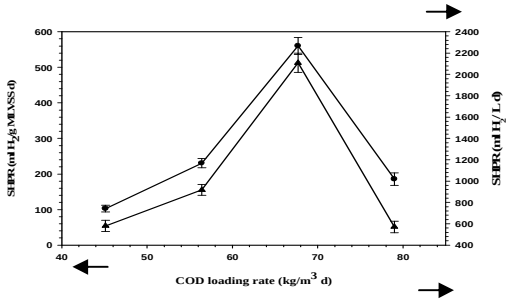
(a)



(b)



(c)



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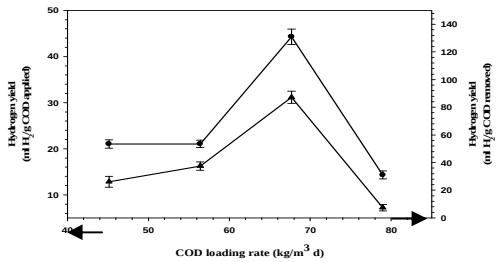

Fig. 2 (a) COD removal efficiency and gas production rate versus COD loading rate at 55°C and pH 5.5, (b) Gas composition and Hydrogen production rate versus COD loading rate and pH at 55°C and pH 5.5, (c) Specific hydrogen production rate (SHPR) versus COD loading at 55°C and pH 5.5, (d) Hydrogen yield versus COD loading rate at 55°C and pH 5.5

$$C_6H_{12}O_6 \longrightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (1)$$

$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 4H_2 + 2CO_2 \quad (2)$$

$$C_6H_{12}O_6 + 2H_2 \longrightarrow CH_3CH_2COOH + 2H_2O \quad (3)$$

Another factor that can affect to hydrogen production performance is ethanol. The ethanol concentration (Figure 3) increased with increasing COD loading rate and attained a maximum value of 5600 mg/l at a COD loading rate 68 kg/m^{3}d. The highest ethanol concentration corresponded to the highest hydrogen production performance (Figure 2c-2d) which is in a good agreement with previous work [28]. The results can be explained by the fact that the produced ethanol can reduce the acidity in the studied reactor, leading to the improvement of the efficiency of hydrogen production.

$$C_6H_{12}O_6+H_2O \longrightarrow C_2H_5OH+CH_3COOH+2H_2+2CO_2 \quad (4)$$

D. Microbial concentration and microbial washout results

The microbial concentration in the bioreactor in terms of MLVSS as a function of COD loading rate is shown in Figure 4. The MLVSS decreased with increasing COD loading rate whereas the microbial washout from the system in terms of VSS increased with increasing COD loading rate. As a further increases COD loading rate, MLVSS slightly increased up to 3800 mg/l while VSS slightly decreased to 2300 mg/l.

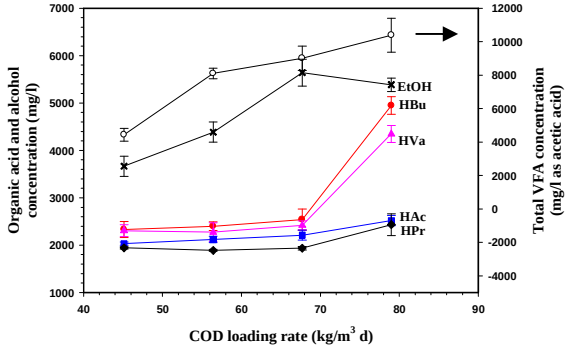

Fig. 3 Total VFA, VFA composition and ethanol concentration versus COD loading rate at 55°C and pH 5.5

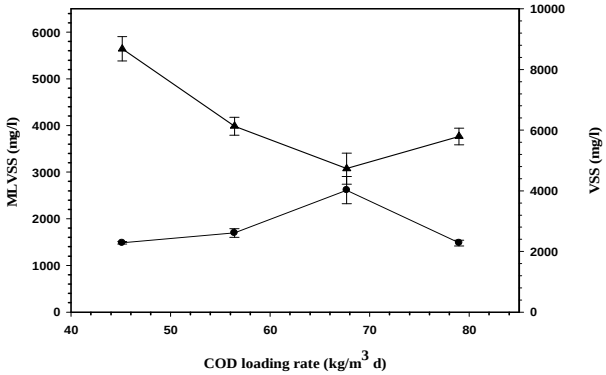

Fig. 4 MLVSS and effluent VSS versus COD loading rate at 55°C and pH 5.5

The results suggest that increasing microbial washout from the system and decreasing microbial concentration in the bioreactor can directly affect the hydrogen production performance of the hydrogen-producing bacteria to utilize organic substrate for growth. For this work, the condition that suitable for hydrogen-producing bacteria growth and the highest hydrogen production performance is at a COD loading rate 68 kg/m^{3}d (Figure 2c-2e) as discussed previously. Shin *et al.*, [8] studied the effect of volatile solid (VS) on hydrogen production. They found that hydrogen production increased with increasing VS concentration because of inactivated methanogenesis by thermophillic condition.

IV. Conclusions

The hydrogen production from alcohol wastewater by anaerobic sequencing batch reactor (ASBR) under thermophillic operation (55 °C), and controlled pH of 5.5 was investigated in this present work and it greatly depended on COD loading rate. Under a COD loading rate of 68 kg/m^{3}d, the system gave the best hydrogen production performance with a maximum specific hydrogen production rate of 525 ml H_2/g MLVSS d and a maximum hydrogen yield of 130 ml H_2/g COD removed.

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REFERENCES

[1] Das D, Veziroglu TN. "Hydrogen production by biological processes: a survey of literature". International Journal Hydrogen Energy, Vol. 26, pp. 13-28, 2001.

[2] Lay JJ, Le YJ, Noike T. "Feasibility of biological hydrogen production from organic fraction of municipal solid waste". Water Research, Vol. 33, pp. 2579-2586, 1999.

[3] Mizuno O, Dinsdale R, Hawkes DL, Noike T. "Enhancement of hydrogen production from glucose by nitrogen gas sparging". Bioresource Technology, Vol. 73, pp.59-65, 2000.

[4] Kapdan IK, Kargi F. "Bio-hydrogen production from waste materials". Enzyme Microbial Technology, Vol. 38, pp. 569-582, 2006.

[5] Mohan SV, Babu VL, Sarma PN. "Anaerobic biohydrogen production from dairy wastewater treatment in sequencing batch reactor (AnSBR): effect of organic loading rate". Enzyme Microbial Technology, Vol. 41, pp. 506-15, 2007.

[6] Han SK, Shin HS. "Biohydrogen production by anaerobic fermentation of food waste". International Journal Hydrogen Energy, Vol. 29pp. 569-577, 2004.

[7] Sreethawong T, Chatsiriwatana S, Rangsunvigit P, Chavadej S. "Hydrogen production from cassava wastewater using an aerobic sequencing batch reactor: Effects of operational parameters, COD:N ratio, and organic acid composition". International Journal Hydrogen Energy, Vol. 35, pp. 4092-4102, 2010.

[8] Shin HS, Youn JH, Kim SH. "Hydrogen production from food waste in anaerobic mesophillic and thermophillic acidogenesis". International Journal Hydrogen Energy, Vol. 29, pp. 1355-1363. 2004.

[9] Arooj MF, Han SK, Kim AH, Kim DH, Shin HS. "Effect of HRT on ASBR converting starch into biologicl hydrogen". International Journal Hydrogen Energy, Vol. 33, pp. 6509-6514, 2008.

[10] Argun H, Kargi F, Kapdan IK, Oztekin R. "Biohydrogen production by dark fermemtation of wheat powder solution: Effects of C/N and C/P ratio on hydrogen yield and formation rate". International Journal Hydrogen Energy, Vol. 33, pp. 1813-1819, 2008.

[11] Chong ML, Sabaratnam V, Shirai Y, Hassan MA. "Biohydrogen production from biomass and industrial wastes by dark fermentation". International Journal Hydrogen Energy, Vol. 34, pp. 3277-3287, 2009.

[12] Lee KS, Hsu YF, Lo YC, Lin PJ, Lin CY, Chang JS. "Exploring optimal environmental factors for fermentative hydrogen production from starch using mixed anaerobic microflora". International Journal Hydrogen Energy, Vol. 32, pp. 1565-1572, 2008.

[13] Wang J, Wan W. "Comparison of different pretreatment methods for enriching hydrogen-producing bacteria from digested sludge". International Journal Hydrogen Energy, Vol. 33, pp. 2934-2941, 2008.

[14] Hawkes FR, Hussy I, Kyazze G, Dinsdale R, Hawkes DL. Continuous dark fermentative hydrogen production by mesophilicmicroflora: Principles and progress. International Journal Hydrogen Energy, Vol. 32, pp. 174-184, 2007.

[15] Lin CY, Hung WC. "Enhancement of fermentative hydrogen/ethanol production from cellulose using mixed anaerobic cultures". International Journal Hydrogen Energy, Vol. 33, pp. 3660-3667, 2008.

[16] Kapdan IK, Kargi F. "Bio-hydrogen production from waste materials". Enzyme Microbial Technology, pp. 38569–53882, 2006.

[17] Cheng J, Su H, Zhou J, Song W, Cen K. "Hydrogen production by mixed bacteria through dark and photo fermentation". International Journal Hydrogen Energy, Vol. 36, pp. 450-457, 2011.

[18] Hwang JH, Choi JA, Shanab RA, Bhatnagar A, Min B, Song H, Kumar E, Choi J, Lee ES, Kim YJ, Umg S, Lee DS, Joen BH. "Effect of pH and sulfate concentration on hydrogen production using anaerobic mixed microflora". International Journal Hydrogen Energy, Vol. 34, pp. 9702-9719, 2009.

[19] Eaton AD, Clesceri LS, Rice EW, Greenberg AE, "Standard Methods for The Examination of Water and Wastewater". American Public Health Association (APHA), American Water Works Association (AWWA) & Water Environment Federation (WEF), Washington, DC, 2005.

[20] Sreethawong T, Niyamapa T, Neramitsuk H, Rangsunvigit P, Leethochawalit M, Chavadej S. "Hydrogen production from glucose-containing wastewater using an anaerobic sequencing batch reactor: Effects of COD loading rate, nitrogen content. And organic acid composition". Chemical Engineering Journal, Vol. 160, pp. 322-332, 2010.

[21] Fang HH, Liu H. "Effect of pH on hydrogen production from glucose by a mixed culture". Bioresource Technology, Vol. 82, pp. 87-93, 2002.

[22] Lin CY, Lay CH. "Effects of carbonate and phosphate concentrations on hydrogen production using anaerobic sewage sludge microflora". International Journal Hydrogen Energy, Vol. 29, pp. 275-281, 2004.

[23] Chen WH, Sung S, Chen SY. "Biological hydrogen production in an anaerobic sequencing batch reactor: pH and cyclic duration effects". International Journal Hydrogen Energy, Vol. 34, pp. 227-234, 2009.

[24] Miyake J. "The science of biohydrogen: an energetic view. In: Zaborsky OR, editor. Biohydrogen". New York: Plenum Press, pp. 7–18, 1998.

[25] Luo G, Xie L, Zou Z, Zhou Q, Wang JY. "Fermentative hydrogen production from cassava stillage by mixed anaerobic microflora: Effects of temperature and pH". Applied Energy, Vol. 87, pp. 3710–3117, 2010.

[26] O-Thong S, Prasertsan P, Intrasungkha, Dhamwichukorn S, Birkeland NK. "Optimization of simultaneous thermophillic fermentative hydrogen production and COD reduction from palm oil mill effluent by *Thermoanaerobacterium*-rich sludge". International Journal Hydrogen Energy, Vol. 33, pp. 1221-31, 2008.

[27] Hawkes FR, Dinsdale R, awkes DL, Hussy I. "Sustainable fermentative hydrogen production: challenges for process optimization". International Journal Hydrogen Energy, Vol. 27, pp. 1339-1347, 2002.

[28] Guo WQ, Ren NQ, Wang XJ, Xiang WS, Meng ZH, Ding J, Qu YY, Zhang LS. "Biohydrogen production from ethanol-type fermentation of molasses in an expanded granular sludge bed (EGSB) reactor". International Journal Hydrogen Energy, Vol. 33, pp. 4981-4988, 2008.