UNIVERSITI PUTRA MALAYSIA

BIOHYDROGEN PRODUCTION FROM PALM OIL MILL EFFLUENT USING A THERMOPHILIC SEMI-CONTINUOUS PROCESS WITH RECYCLING

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia
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Chairman: Professor Fakhru'l-Razi Ahmadun, PhD.

Faculty: Engineering

The effluent resulted from the palm oil industry can cause serious pollution if left untreated. This is a problem of considerable magnitude, notably in Malaysia. Anaerobic biological treatment processes, have effectively used to treat POME. Currently, methane production is the most commonly used method to treat POME, but hydrogen production is an innovative alternative because of the methane green house nature. Processes under thermophilic anaerobic conditions showed superior production rates and less variety in fermentation by products which is economically and technically interesting.

A fermentation process for hydrogen production by anaerobic micro flora under controlled conditions (pH 5, T 60^{o}C and 200rpm) in a semi-continuous process with recycling was developed for this study. The substrate used in this study was POME (Palm Oil Mill Effluent) and POME sludge for the biogas production was collected to be used as source of inocula. The experimental setup conducted using a 5-L fermenter and six steady states

were achieved. The POME sludge possessed a maximum hydrogen evolution rate of 0.83 L H2 gas/Lmed.hr at the fifth steady state with a maximum hydrogen percentage in the biogas of 64% at the fourth steady state.

Increasing the organic loading rate from 10.3 to 25.5 kgCOD/m3/d resulted in increasing biomass productivity up to 25.325 g/L at the sixth steady associated with increasing biogas emission throughout the six steady states, and an increase in the total gas yield up to 0.97 L gas/gCOD/d at the fifth steady state. It is also noted that increasing the organic loading rates resulted in increasing hydrogen yield up to 0.6 L gas/g COD/d at the fifth steady state, and decreasing the COD removal efficiencies from (66.33 to 59.32%) throughout the system, this might be due to the decrease of hydraulic retention time (HRT) and solids retention time (SRT) from 5 to 2.94 days and 52.282 to 12.260 days, respectively. The minimum solids retention time ($SRT_{m)}$ for this study was 1.99 days.

A mathematical model was developed to understand the kinetics of the digester operations. The growth yield coefficient, Y and the specific microorganism death rate, k_d for anaerobic semi-continuous system, were found to be 0.3075 (gVSS/gCOD) and 0.1035 day^{-1} respectively. The maximum specific growth rate, μ_{max} , maximum substrate utilization rate, K, half-velocity coefficient, K_s for the process were found to be 0.502369 day-1,

1.63372gCOD/gVSS.day, 50.336546 mgCOD/l respectively. This study suggests that using thermophilic semi-continuous process with recycling is suitable for hydrogen production from POME and POME biomass and increasing the organic loading rate esulted in an increase of biogas production throughout the system.

Abstrak tesis yang dikemukakan kepada senat Universiti Putra Malaysia sebagai memenuhi syarat keperluan untuk ijazah Sarjana Sains

PENGHASILAN BIOHIDROGEN DARIPADA SISA BUANGAN KILANG KELAPA SAWIT MELALUI PROSES SEPARA SELANJAR TERMOFILIK DENGAN KITAR SEMULA

Oleh

SUKAINA F.A. BARGHASH

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Sisa buangan hasil daripada industri minyak kelapa sawit boleh menyebabkan pencemaran yang serius jika dibiarkan tanpa dirawat. Masalah ini juga dianggap penting terutama di Malaysia. Proses-proses rawatan biologikal anarobik telah digunakan dengan baik bagi merawat POME. Pada masa ini, penghasilan metana merupakan kaedah yang paling lazim digunakan bagi merawat POME, tetapi penghasilan hidrogen pula merupakan alternatif baru disebabkan metana merupakan gas rumah hijau yang semulajadi. Proses-proses di bawah keadaan anarobik termofilik telah menunjukkan kadar penghasilan yang amat baik serta kurangnya penghasilan pelbagai produk sampingan di dalam proses fermentasi yang mana amat memberangsangkan daripada segi ekonomi dan teknikal. Proses fermentasi bagi penghasilan hidrogen oleh mikroflora anarobik pada keadaan terkawal (pH 5, suhu 60^{o}C dan 200rpm) di dalam proses separa selanjar dengan kitar semula telah dibangunkan untuk kajian ini. Substrat

yang telah digunakan di dalam kajian ini adalah POME (sisa buangan kilang kelapa sawit) manakala enapcemar POME bagi penghasilan gas-bio telah diambil untuk digunakan sebagai sumber inokula. Eksperimen dijalankan dengan menggunakan fermenter 5-L dan enam keadaan mantap telah dicapai. Enapcemar POME telah mencapai penghasilan hidrogen maksima pada kadar 0.83 L H_2 gas/Lmed.hr pada keadaan mantap yang kelima dengan peratusan hidrogen maksima di dalam gas-bio pada 64% pada keadaan mantap yang keempat.

Peningkatan kadar berat organik daripada 10.3 ke 25.5 kgCOD/m^3/d menyebabkan peningkatan produktiviti biomas sehingga 25.325 g/L pada keadaan mantap keenam selari dengan peningkatan pancaran gas-bio sepanjang keenam-enam keadaan mantap, dan hasil gas keseluruhan juga meningkat sehingga 0.97 L gas/gCOD/d pada keadaan mantap kelima. Didapati juga peningkatan kadar berat organik menyebabkan peningkatan hasil hidrogen sehingga 0.6 L gas/g COD/d pada keadaan mantap kelima, dan penurunan keberkesanan pengurangan COD daripada (66.33 ke 59.32%) di sepanjang sistem, ini mungkin disebabkan penurunan masa bertahan hidraulik (HRT) dan masa bertahan pepejal (SRT) masing-masing daripada 5 ke 2.94 hari dan 52.282 ke 12.260 hari. Masa bertahan pepejal minima (SRT_m) bagi kajian ini adalah pada 1.99 hari.

Satu model matematik telah dikembangkan untuk memahami kinetik bagi operasi proses tersebut. Pekali kadar pertumbuhan Y dan kadar penguraian mikroorganisma spesifik k_d bagi sistem separa selanjar anarobik telah diperolehi masing-masing pada nilai 0.3075 (gVSS/gCOD) dan 0.1035 d^{-1}. Kadar maksima pertumbuhan spesifik μ_{max}, kadar maksima penggunaan substrat K, pekali separuh halaju K_s bagi proses telah diperolehi masing-masing pada nilai 0.502369 d^{-1}, 1.63372gCOD/gVSS.d dan 50.336546 mgCOD/l. Kajian ini mencadangkan bahawa penggunaan proses separa selanjar termofilik dengan kitar semula adalah sesuai bagi penghasilan hidrogen daripada POME dan biomas POME serta peningkatan kadar berat organik didapati meningkatkan penghasilan biogas bagi keseluruhan sistem.

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I certify that an Examination Committee has met on   to conduct the final examination of Sukaina F. A. Barghash on her MS.C. thesis entitled "Biohydrogen synthesis from Palm Oil Mill Effluent POME and POME biomass by anaerobic fermentation using thermophilic semi-continuous process with recycling" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

SUKAINA F. A. BARGHASH

Date

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CHAPTER 5

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CONCLUSION AND RECOMMENDATION

5.1 Introduction

This chapter has two sections. The first presents conclusion of the study, whereas the second provides recommendations for future work.

5.2 Conclusions

The study conclusions can be summarized as follows:

1) The increasing rates of biomass was associated with an increase in biogas emission throughout six steady states, and an increase in the total gas yield up to 0.97 L gas/gCOD/d at the fifth steady state.
2) The COD removal efficiencies decreases from (66.33 to 59.32%) when the organic loading rates increased from 10.3 to 25.5 kgCOD/m^3/d , this might be due to the decreasing hydraulic retention time (HRT) and solids retention time (SRT) from 5 to 2.94 days and 52.282 to 12.260 days, respectively. which means less time was given for the bacteria to digest the organic material.
3) Increasing the organic loading rates has increased the hydrogen yield up to 0.6 L gas/g COD/d at the fifth steady state.

4) The hydrogen percentage in the biogas fluctuated throughout the six steady states. It ranged from (61.5 to 64.75%). That was because different microorganisms participate in the biological hydrogen processes, these processes depend mainly on the presence of hydrogen producing enzymes which catalyze the chemical reaction and the ability or the natural activity of these enzymes could limit the overall process.
5) The increase in SRT caused a decrease in S, the effluent waste concentration.
6) When the average of SRT decreases from 52.28 to 12.26 days; the average COD removal efficiency decreases from 66.33 to 59.32%.
7) The bacterial population has not totally utilized the substrate supplied to the system. More distinctively, the actual substrate available and substrate utilized per unit biomass are represented by the biological loading rate (BLR) and specific substrate utilization rate (SSUR), respectively.
8) The bacterial concentration increased with decreasing HRT, this may implies that the bacterial growth rate (μ) has an inverse relationship with HRT in a semi-continuous process reactor.
9) The POME sludge possessed significant capacity to transform the organic material in the POME into hydrogen, and produced hydrogen with a maximum evolution rate of 0.83 L H2 gas/Lmed.hr at the fifth steady state.

10) The minimum solids retention time (SRT_m) for this study was 1.99 days. If the value of the solid retention time was lower than the (SRT_m), no sufficient time is allowed for the reaction inside the reactor, no steady state to be achieved and the fermentative process will fail.

11) The growth yield coefficient, Y and the specific microorganism death rate, k_d for anaerobic semi-continuous system, were found to be 0.3075 (gVSS/gCOD) and 0.1035 day^{-1} respectively.

12) The maximum specific substrate utilization rate, K ; half-velocity coefficient, K_s and maximum specific growth rate, μ_{max} were found to be 1.63 gCOD/gVSS/d, 50.33 gCOD/L, and 0.502 d^{-1} respectively.

5.3 Recommendations

The use of thermophilic semi-continuous process with recycling to produce hydrogen by anaerobic fermentation has produced consistent results. Therefore, under appropriate conditions, anaerobic microflora in the POME could be proposed as the most suitable microorganism for the production of hydrogen from biomass resources without sterilization. The conversion of renewable biomass to hydrogen has an important role for future energy production.

It is possible to apply higher OLR to the anaerobic semi-continuous process with recycling system, to observe the effect of organic loading rate on effluent substrate concentration and biohydrogen production.

Future work should be conducted on applying higher organic loading rates to the system to study and see their influence on the biogas production. Also, study the influence of increasing the working volume on the process performance.

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CHAPTER 4

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RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results of this study on the palm oil mill effluent and biomass in an anaerobic fermentative thermophilic process using semi-continuous mode with recycling to produce hydrogen gas and study the reproducibility and stability of the anaerobic micro flora in the palm oil mill effluent sludge, also to evaluate the microbial kinetics for growth and substrate utilization rate**.** This study was conducted using a 5 liter bioreactor.

The proposed utilization of POME as a medium for microbial growth to produce hydrogen, has been made based mainly on the non-toxic and complete biodegradability nature of the effluent and the fact that it contains almost all the necessary nutrients for the anaerobic production process (Chin *et al*., 1996). POME had always been considered as a financial burden to the palm oil industry because of the very high capital cost of its treatment systems (Ma *et al*., 1988), and it has been found to be a resource from which valuable products can be obtained through intensified research and development efforts over the years. There are many beneficial options for the palm oil industry. All these options involve an integrated approach where all the waste products are beneficially utilized.

4.2 Semi-continuous process

The aim of this study was to develop a fermentation process for hydrogen production by anaerobic microflora addresses both engineering and microbial aspects.

This study was based on many previous studies that involved using palm oil mill effluent as substrate to produce hydrogen (Morimoto *et al*., 2004; Yassin *et al*., 2004; Atif *et a*l., 2004; 2005) using batch and fed batch processes. Previous studies obtained encouraging results in terms of treating the palm oil mill effluent since it is one of the most polluting agro-wastes in Malaysia, coupled with hydrogen production and COD reduction efficiency up to 80-86% (Cheong *et al*., 2004).

Thermophilic semi-continuous anaerobic processes to digest palm oil mill effluent were used in previous studies (Cail and Barford, 1985; Borja and Banks, 1993).

In this study, hydrogen production was carried out in anaerobic fermentative thermophilic process using semi-continuous mode with recycling (Figure 3.4) under controlled conditions of pH, temperature and agitation (pH 5.5, 60 ^{o}C temperature and 200 rpm). The start-up of the fermenter was on batch mode, and was changed to semi-continuous mode, after the gas emission started.

In order to deactivate methanogens, low pH and high temperature are favorable (Mornimoto *et al*., 2004). Control pH to the optimum value is important to enhance hydrogen production, maintain continuous hydrogen production and not to cause hydrogen production inhibition or microbial population shifting which might results in cessation of hydrogen production. The pH, temperature and agitation were controlled and monitored by the computerized set up shown in Appendix A. The pH control was done by feeding certain amounts of HCL and NaOH to the fermenter by the peristaltic pump attached to the fermenter whenever the pH fall below or rise above 5.5 . The temperature was controlled to maintain 60 ^{o}C and the agitation speed was also maintained 200 rpm.

Temperatures between 50-60 ^{o}C and pH range 5-6, were observed to be the optimum temperature and pH for production of hydrogen (Taguchi *et al*., 1994; Ueno *et al*., 2001a). Maximum hydrogen production using palm oil mill effluent as substrate occurred at a pH range of 5.5-6 (Yassin *et al*., 2004). Fang and Liu 2002, found that the biogas was free of methane at pH 5.5 or lower due to the suspension of methanogenic activity under acid condition and hydrogen production could be inhibited if the pH is not maintained in the desired range.