ABSTRACT

The effects of various pretreatment methods on the enrichment of H_2 evolving bacterial population and their hydrogen production efficiency using palm oil mill effluent (POME) as substrate were studied. Heat shock pretreatment was shown to be the most effective in enhancing the biological H_2 production. Up-flow anaerobic sludge blanket fixed film (UASB-FF) bioreactor is a modern bioreactor and was used to generate of biological hydrogen with the help of granulated microbial aggregates. A lab scale UASB-FF bioreactor (2.55 lit) with an external settling tank was successfully designed and operated for biohydrogen production from POME. The use of packing media in the middle portion reduced loss of biomass due to flotation associated with poorly performing UASB reactors. The bioreactor was developed in order to shorten the start-up period at low hydraulic retention time (HRT). The organic loading was gradually increased from 4.68 to 51.8 g COD/l.d during this period. Granular sludge was found to develop rapidly within 22 days with an increase in size of granules from an initial pinpoint size to about 1 mm. A marked improvement in shortening reactor start-up period (22 days) was achieved with 42.5 % COD removal at an OLR of 51.8 g COD/l.d.

Experiments of fermentation hydrogen production of POME were conducted based on a central composite face-centered design (CCFD) and modeled and analyzed with two variables i.e. feed flow rate (Q_F) and up-flow velocity (V_{up}) using response surface methodology (RSM). The optimum conditions for the fermentation hydrogen production of the pre-settled POME were between Q_F of 3.71 l/d, V_{up} of 1.48 m/h and Q_F of 2.03 l/d, V_{up} of 2.31m/h, respectively. The experimental findings were in close agreement with the model prediction. The proposed kinetic equations and a simplified Monod’s model were successfully employed to describe the kinetics of fermentation hydrogen production from POME in the UASB-FF bioreactor. The maximum hydrogen

production rate and hydrogen yield were 0.306 l H_2/g $COD_{removed}$.d and 0.310 l H_2/g COD, respectively. The maximum specific growth rate (μ_{max}) of hydrogenesis bacteria grown on POME as substrate, the half-velocity constant (*K*s), were calculated at 0.371 d^{-1} (38 °C) and 10.9 g/L, respectively, when POME concentration was 15.0 g/L. In this study, the kinetic parameters *Y*, K_d, and *k* were obtained 0.093 g/g, 0.0046 d^{-1}, and 3.99 g COD/g VSS.d, respectively.

In a batch experiment, Effects of three important variables *viz.* initial COD concentration (COD_{in}), biomass concentration and initial bicarbonate alkalinity (BA) on biological hydrogen production from POME using the granulated sludge were also investigated. The maximum specific hydrogen production rate (55.42 mmol H_2/g VSS.d) was at the COD_{in}, MLVSS and initial BA of 6500 mg/l, 2000 mg/l and 1100 mg $CaCO_3$/L, respectively. The maximum hydrogen yield (124.5 mmol H_2/g $COD_{removed}$) was also occurred at the COD_{in}, MLVSS and initial BA of 3000 mg/l, 4000 mg/l and 1100 mg $CaCO_3$/L, respectively. The minimum initial bicarbonate alkalinity required was determined to be 0.17 g $CaCO_3$ per gram initial COD. The results of mass transfer study demonstrated that substrate mass transfer into granules was not a limiting factor in POME anaerobic fermentation by the microbial granules.

All cumulative hydrogen production was well correlated to the modified Gompertz equation with R^2 more than 0.99. The kinetic parameters for total accumulated hydrogen production (ml) were *P*: 329.8 ml, R_{max}: 83.5 ml H_2/h and λ: 5.45 h.

Abstrak

Kesan pelbagai pra-rawatan bagi meningkatkan hasilan gas hidrogen yang melibatkan populasi bakteria dan produksi hidrogen yang efisyen menggunakan air sisa kilang kelapa sawit (POME) sebagai substrat telah dikaji. Pra-rawatan kejutan haba merupakan rawatan paling berkesan bagi meningkatkan hasilan gas hidrogen secara biologi. Bioreaktor "Up-flow anaerobic sludge blanket fixed film" (UASB-FF) digunakan untuk menghasilkan hidrogen secara biologi dengan bantuan granul mikrob agregrat. Satu bioreaktor UASB-FF skala makmal (2.55 l) dengan tangki pengenapan luaran telah direka dan dioperasi untuk menghasilkan hidrogen daripada penapaian POME. Bioreaktor gigunakan untuk memendekkan tempoh masa pemulaan masa retensi hidraulik (HRT). Beban organik dipertingkatkan secara beransur-ansur dari 4.68 kepada 51.8 g COD/l.d. hari dalam jangka masa ini. Granul enapcemar didapati membesar dengan cepat dalam tempoh masa 22 hari dengan peningkatan saiz granul bermula daripada saiz titik pin kepada kira-kira 1 mm.

Penghasilan hidrogen daripada penapaian POME telah dijalankan berdasarkan "central composite face-centered design" (CCFD) dan dimodel dan dianalisis menggunakan dua pembolehubah; iaitu kadar aliran (Q_F) dan halajo aliran ke atas (V_{up}) menggunakan Metodologi Respos Permukaan (RSM). Keadaan optimum untuk fermentasi penghasilan hidrogen dari pra-enapan POME adalah di antara Q_F 3.71 l/hari, V_{up} 1.48 m/jam dan Q_F 2.03 l/hari, V_{up} 2.31 m/jam. Keputusan eksperimen menepati baik ramalan model. Persamaan kinetik dan model Monod yang dipermudahkan menerangkan dengan baik kaedaan kinetik fermentasi penghasilan hidrogen daripada POME dalam bioreaktor UASB-FF. kadar penghasilan hidrogen maksimum dan hasilan hidrogen adalah 0.306 l H_2/g COD dikeluarkan hari dan 0.310 l H_2/g COD mesing-masing. Kadar pertumbuhan spesifik (μ_{max}) bakteria hidrogenesis menggunakan POME

sebstrat, pemalar halaju separa (Ks), bernilai 0.371 hari^{-1} (38˚C) dan 10.9 g/l masing-masing, apabila kepekatan POME adalah 15.0 g/l. Dalam kajian ini, parameter kinetik Y, K_d, dan k didapati bernilai 0.093 g/g, 0.0046 d^{-1}, dan 3.99 g COD/g VSS.hari, masing-masing.

Dalam eksperimen kelompok, kesan tiga pembolehubah yang penting, iaitu kepekatan masuk COD (COD_{masuk}), kepekatan biojisim dan alkalinity awal bikarbonat (BA) ke atas penghasilan hidrogen spesifik yang maksimum (55.42 mmol H_2/g VSS.hari) kerlaku apabila COD_{masuk}, MLVSS, dan BA awal bernilai 6500 mg/l, 2000 mg/l, dan 1100 mg $CaCO_3$/ l masing-masing. Penghasilan hidrogen maksimum (124.5 mmol H_2/g $COD_{dikeluarkan}$) iuga berlaku apabila COD_{masuk}, MLVSS, dan BA awal bernilai 3000 mg/l, 4000 mg/l, dan 1100 mg $CaCO_3$/ l masing-masing. Semua produksi hidrogen kumulatif dapat dikaitkan dengan baik oleh persamaam Gompertz yang telah dimodifikasikan dengan nilai R^2 melbili 0.99. Parameter-parameter kinetik untuk jumlam penghasilan hidrogen terkupul (ml) adalah P: 329.8 ml, R_{max}: 83.5 ml H_2/ jam dan λ: 5.45 jam.

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LIST OF ABBREVIATION

2FI	Two factor interaction
AF	Anaerobic filter
Alk	Alkalinity
AnFBR	Anaerobic fluidized-bed reactor
ANOVA	Analysis of variance
ASBR	Anaerobic sequencing batch reactor
BA	Bicarbonate alkalinity
BOD	Biochemical oxygen demand
CCD	Central composite design
CCFD	Central composite face-centered design
COD	Chemical oxygen demand
COD_{eff}	Effluent chemical oxygen demand
COD_{in}	Influent chemical oxygen demand
CPO	Crude palm oil
CV	Coefficient of variance
DoE	Design of experiment
E(t)	Distribution of the exit times
F(t)	Cumulative residence time distribution function
FFB	Fresh fruit bunch
F/M	Food to microorganism
GSS	Gas solids separator
HRT	Hydraulic retention time
HPR	Hydrogen production rate
MDI	Morrill Dispersion Index
MLVSS	Mixed liquor volatile suspended solids

OLR	Organic loading rate
P	Probability of error
POME	Palm oil mill effluent
R^2	Coefficient of determination
RSM	Response surface methodology
SCOD	Soluble chemical oxygen demand
SD	Standard deviation
SEM	Scanning electron microscopy
SHPR	Specific hydrogen production rate
SRT	Solid retention time
SVI	Sludge volume index
TA	Total alkalinity
TCOD	Total chemical oxygen demand
TKN	Total Kjeldahl nitrogen
TSS	Total suspended solids
TVFA	Total volatile fatty acids
UASB	Up-flow anaerobic sludge blanket
UASB-FF	Up-flow anaerobic sludge blanket fixed film
UFF	Up-flow fixed film
VFA	Volatile fatty acids
VSS	Volatile suspended solids

LIST OF SYMBOLS

		Unit
C	Ideal flow concentration	(mM)
C_0	Initial flow concentration of the tracer	(mM)
C_i	Concentration at *i*th measurement	(mmol/l)
H(*t*)	Cumulative hydrogen production	(ml)
k	Transportation rate constant into the granule	(d^{-1})
K_s	Half-velocity constant	(g COD/l)
P	Hydrogen production potential	(ml)
Q_e	Effluent flow rate	(l/d)
Q_F	Feed flow rate	(l/d)
Q_g	Biogas production rate	(l/d)
Q_H	Volume of gas produced per day	(l H_2/d)
R	Maximum hydrogen production rate	(ml/h)
S_0	Influent substrate concentration	(g COD/l)
S	Effluent substrate concentration	(g COD/l)
t	Hydraulic retention time	(d)
t_i	Time at *i*th measurement	(min)
V	Volume of the reactor	(lit)
V_{up}	Up-flow velocity	m/h
X	Biomass concentration	(mg/l)
X_e	Effluent VSS concentration	(mg/l)
X_i	Independent variables / factors	(-)
Y_i	Response	(-)
Y_H	Hydrogen yield constant	(l H_2/g $COD_{removed}$.d)
Y_x	Growth yield constant	(g VSS/g $COD_{removed}$.d)

Greek symbols

α	Distance from the centre of the design space to axial point	(-)
β_0	Constant coefficient	(-)
β_i	Coefficients for the linear effect	(-)
β_{ii}	Coefficients for the quadratic effect	(-)
β_{ij}	Coefficients for the cross-product effect	(-)
η	Effectiveness factor	(-)
μ	Specific microbial growth rate	(d^{-1})
μ_m	Maximum specific microbial growth rate	(d^{-1})
λ	Lag phase time	(h)
λ_{max}	Maximum absorption	(nm)
τ	Theoretical retention time	(min)
$\bar{t}_{\Delta c}$	Mean detention time	(min)
Δt_i	time increment about C_i	(min)
$\Delta\tau$	Deviations from the ideal retention time	(min)