UNIVERSITI PUTRA MALAYSIA

ENHANCED BIOMETHANATION OF PALM OIL MILL EFFLUENT DURING ANAEROBIC TREATMENT IN A CLOSED DIGESTER TANK

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the requirements for the Degree of Doctor of Philosophy

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Chairman : Professor Mohd. Ali Hassan, PhD

Faculty : Engineering

The methane capture project from anaerobic treatment of palm oil mill effluent (POME) treatment for clean development mechanism (CDM) is becoming increasingly important due to the problems caused by the utilisation of fossil fuels such as global warming, air and water pollution, resource depletion, high energy price, acid rain and others. The traditional way of treating POME using large open ponds or tanks system is an unsustainable practice because large amounts of methane are released to the atmosphere contributing to the greenhouse gas (GHG) emission. By closing the digester, methane could be captured and utilized to generate electricity for internal consumption or Tenaga Nasional Berhad (TNB) grid connection. Moreover, with CDM registration with the United Nation Framework Convention on Climate Change (UNFCCC), the captured methane could be converted into carbon credit and could be traded in the international market as certified emission reduction (CER). Hence, there is an urgent requirement for the industry to capture as much methane as possible so that higher

CER and electricity power could be generated to partly finance the overall project cost. For this purpose there is an urgent need to understand the various operational conditions that contribute to the improved methane production in terms of methane yield and productivity without affecting the organic removal efficiency such as accelerated start-up process, effect of higher sludge recycling rate, effect of mixing and effect of co-digestion.

In chapter 4, the accelerated start-up process of the closed digester tank (CDT) was achieved by transfer the seed sludge from either top or bottom of the open digester tank (ODT). The bottom seed sludge transfer process led to better results including a 24 day start-up period, stable pH condition (pH 6.8-7.2), high COD removal efficiency (>90%), satisfactory VFA to Alk ratio (<0.3) and satisfactory biogas production of nearly 1.8 kg m^{-3} d^{-1} with methane composition of 50 to 60%. The presence of high amount of methanogens in the seed sludge was able to reduce the long acclimatization period and the CDT could be fed with POME within less than a day after the transfer process was completed. Scanning electron microscopy (SEM) and fluorescence in situ hybridization (FISH) pictures revealed abundant amounts of bacteria and methanogens, in particular *Methanosaeta* sp. in the seed sludge samples which are very important for the biomethanation process.

In chapter 5, the effect of higher sludge recycling rate was studied by applying organic loading rates (OLR) (between 1.0 and 10.0 kgCOD m^{-3} d^{-1}) at different sludge recycling rates (6 m^3 d^{-1}, 12 m^3 d^{-1} and 18 m^3 d^{-1}). At sludge recycling rate of 18 m^3 d^{-1}, the maximum OLR achieved was 10.0 kgCOD m^{-3} d^{-1} with biogas and methane productivity of 1.5 m^3 m^{-3} d^{-1} and 0.9 m^3 m^{-3} d^{-1}, respectively. By increasing the sludge recycling rate, the VFA concentration accumulated inside the CDT was controlled below its inhibitory limit (1000 mg L^{-1}) and the COD removal efficiency recorded was above 95%. Two methanogens species (*Methanosarcina sp.* and *Methanosaeta concilii)* have been identified from sludge samples obtained from the digester and recycled stream. By increasing the sludge recycling rate upon treatment at higher OLR, the treatment process was kept stable with high COD removal efficiency.

In chapter 6, the effect of mixing was studied by applying four different mixing regimes i.e natural mixing (NM), minimal horizontal mixing (MHM), minimal horizontal and vertical mixing (MHVM) and vigorous mixing (VM) in the CDT. The COD removal efficiency recorded satisfactory result (> 90%) when subjected to the first three mixing regimes but reduced to the lowest of 85% when VM was applied. In the NM, MHM and MHVM experiments, the maximum VFA concentration in the CDT were recorded below the critical level of 1000 mg L^{-1}. The MHM gave the highest methane productivity at 1.4 m^3 m^{-3} d^{-1} in comparison to NM at 1.0 m^3 m^{-3} d^{-1} and MHVM at 1.1 m^3 m^{-3} d^{-1}. This indicates MHM was sufficient for contact between substrate and microorganisms and to release the entrapped biogas inside the CDT. In contrast, VM was found to inhibit the methane production process VFA concentration was recorded high at 3700 mg L^{-1}. The high VFA concentration have disrupted the syntrophic relationship between acidogens and methanogens and inhibited the methanogenesis.

In chapter 7, the effect of co-digestion of POME and RGWW under mesophilic condition at different RGWW percentages (1.0-5.25%). The digester performance in terms of COD removal efficiency and methane production rate and stability were evaluated. At 1.0% of RGWW co-digested, both COD removal efficiency and methane production rate showed satisfactory results with higher than 90% and 505 m^3 d^{-1}, respectively. However, once the percentage was increased to a maximum of 5.25%, COD removal efficiency remains high but the methane production rate reduced to 307 m^3 d^{-1}. At this stage, the digester became unstable due to high VFA concentration of 913 mg L^{-1} and low cells concentration of 8.58 g L^{-1} inside the digester. This was due to the effect of plasmolysis on the methanogens at high NaCl concentration. Thus co-digesting of RGWW with high NaCl content and POME is satisfactory for COD removal but not for increasing the methane production.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENINGKATAN BIOMETANASI EFLUEN KILANG SAWIT SEMASA RAWATAN ANAROBIK DI DALAM TANGKI PENCERNA TERTUTUP

Oleh

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April 2010

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Projek memerangkap metana daripada rawatan anaerobik effluen kilang sawit bagi mekanisma pembangunan bersih (CDM) semakin penting di dalam industri sawit disebabkan oleh masalah penggunaan bahan bakar fosil seperti pemanasan global, pencemaran air dan udara, pengurangan sumber, harga tenaga yang mahal hujan asid dan lain-lain. Kaedah tradisional merawat effluen kilang sawit menggunakan kolam terbuka atau tangki adalah amalan yang tidak lestari kerana membebaskan sejumlah besar metana ke persekitaran dan seterusnya menyumbang kepada gas rumah hijau. Dengan menggunakan tangki pencerna anarobik tertutup, metana boleh diperangkap dan digunakan untuk menjana elektrik samada untuk penggunaan kilang atau disambungkan ke grid Tenaga Nasional Berhad. Tambahan pula dengan pendaftaran CDM dengan Persidangan Rangkakerja Bangsa-Bangsa Bersatu ke atas Perubahan Cuaca (UNFCCC), metana yang diperangkap boleh ditukar menjadi karbon kredit yang boleh

didagangkan di pasaran antarabangsa sebagai pengurangan pembebasan yang diperakui (CER). Ini mewujudkan keperluan yang segera bagi pihak industri meningkatkan pemerangkapan metana untuk meningkatkan CER dan juga penjanaan kuasa elektrik bagi membiayai sebahagian daripada kos projek. Bagi tujuan ini, adalah penting untuk memahami pelbagai kondisi operasi yang menyumbang kepada peningkatan pengeluaran metana di dalam bentuk hasilan metana dan produktiviti tanpa memberi kesan kepada kecekapan penyingkiran organic seperti proses permulaan pantas, kesan kadar kitar-semula enapcemar yang tinggi, kesan pencampuran, dan kesan pencernaan bersama.

Di dalam bab 4, proses permulaan pantas telah berjaya dicapai dengan pembenihan langsung dengan memindahkan enapcemar samada daripada bahagian atas ataupun bawah tangki pencerna terbuka. Pemindahan benih enapcemar bahagian bawah menghasilkan keputusan lebih baik termasuk tempoh permulaan singkat 24 hari, keadaan pH stabil (pH 6.8-7.2), kecekapan penyingkiran keperluan oksigen kimia yang tinggi (>90%), nisbah asid lelemak meruap dan kealkalian yang memuaskan (<0.3), pengeluaran gas-bio yang memuaskan hampir kepada 1.8 kg m^{-3} h^{-1} dan komposisi metana 50 ke 60%. Kehadiran jumlah metanogen yang banyak di dalam benih enapcemar telah berjaya memendekkan tempoh ubah-suai aklimitasi dan pencerna boleh disuap dalam masa kurang sehari selepas selesai proses pemindahan benih enapcemar. Mikroskopi pengimbas elektron dan hibridisasi kalimantan setempat (FISH) menunjukkan jumlah bakteria dan metanogen yang banyak terutamanya

Methanosaeta sp., di dalam sampel benih enapcemar yang amat penting untuk proses biometanasi.

Di dalam bab 5, kesan kadar kitar-semula enapcemar yang tinggi telah dikaji dengan menggunakan kadar bebanan organik (OLR) (di antara 1.0 and 10.0 kgCOD m^{-3} j^{-1}) pada kadar kitar-semula yang berbeza (6 m^3 j^{-1}, 12 m^3 j^{-1} and 18 m^3 j^{-1}). Pada kadar kitar-semula 18 m^3 j^{-1}, maksimum OLR yang dicapai adalah 10.0 kgCOD m^{-3} j^{-1}, dengan produktiviti gas-bio dan metana adalah 1.5 m^3 m^{-3} j^{-1} and 0.9 m^3 m^{-3} j^{-1}, masing-masing. Dengan meningkatkan kadar kitar-semula, kepekatan VFA terkumpul di dalam CDT berjaya dikawal di bawah paras terencat (1000 mg L^{-1}) dan kecekapan penyingkiran COD direkodkan melebihi 95%. Dua spesis metanogen (*Methanosarcina sp.* dan *Methanosaeta concilii*), telah dikenalpasti daripada sampel enapcemar diperolehi di dalam pencerna dan aliran kitar-semula. Dengan meningkatkan kadar kitar-semula pada tahap OLR yang tinggi, proses rawatan dapat disetabilkan dengan kecekapan penyingkiran COD yang tinggi.

Di dalam bab 6, kesan pencampuran telah dikaji pada 4 rejim pencampuran yang berbeza; pencampuran semulajadi (NM), pencampuran minima melintang (MHM), pencampuran minima melintang dan menegak (MHVM) dan pencampuran kuat (VM). Kecekapan penyingkiran COD merekodkan keputusan memuaskan lebih tinggi daripada 90% pada rejim pencampuran tiga yang pertama tetapi menurun ke paras terendah 85% apabila VM digunakan. Di dalam ujikaji NM, MHM and MHVM, kepekatan VFA direkodkan di bawah paras kritikal 1000 mg L^{-1}. MHM memberikan produktiviti tertinggi pada 1.4 m^3 m^{-3} j^{-1} dibandingkan dengan NM pada 1.0 m^3 m^{-3} j^{-1} dan MHVM at 1.1 m^3 m^{-3} j^{-1}. Ini menunjukkan MHM sudah memadai untuk menghubungkan makanan dan mikroorganisma dan membebaskan gas-bio yang terperangkap di dalam CDT. Sebaliknya di dalam ujikaji VM didapati pengeluaran metana terencat di mana tiada metana dihasilkan dan kepekatan asid lelemak meruap yang tinggi direkodkan pada 3700 mg L^{-1}. Tahap VFA yang tinggi telah menggangu hubungan sintropik di antara asidogen dan metanogen dan seterusnya merencatkan metanogenesis.

Di dalam bab 7, kesan pencernaan bersama POME dan RGWW telah dikaji. dalam keadaan mesofilik dan peratusan RGWW yang berbeza (1.0-5.25%). Pencapaian pencerna dalam bentuk kecekapan penyingkiran COD dan kadar pengeluaran metana dan kestabilan pencerna telah dinilai. Pada 1.0% RGWW dicerna bersama, kecekapan penyingkiran COD dan pengeluaran metana menunjukkan keputusan memuaskan dengan nilai lebih tinggi daripada 90% dan 505 m^3 j^{-1}, masing-masing. Walaubagaimanapun, apabila peratusan dinaikkan ke paras maksima 5.25%, kecekapan penyingkiran COD kekal tinggi tetapi kadar pengeluaran metana turun mengejut pada 307 m^3 j^{-1}. Pada peringkat ini, pencerna telah menjadi tidak stabil dengan VFA yang tinggi sebanyak 913 mg L^{-1} dan kepekatan sel yang rendah sebanyak 8.58 g L^{-1}. Ini telah disebabkan oleh kesan plasmalisis ke atas metanogen pada kepekatan natrium klorida yang tinggi. Oleh itu pencernaan bersama RGWW berkepekatan NaCL tinggi dengan POME hanya memuaskan kadar penyingkiran COD dan tetapi bukannya meningkatkan pengeluaran metana.

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I certify that a Thesis Examination Committee has met on 1 April 2010 to conduct the final examination of Alawi Bin Hj. Sulaiman on his thesis entitled "Enhanced Biomethanation of Palm Oil Mill Effluent During Anaerobic Treatment in a Closed Digester Tank" in accordance with the Universities and University Colledges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or any other institution.

ALAWI BIN HJ SULAIMAN

Date: 1 April 2010

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APPENDICES