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RICE STRAW WASHWATER WITH UREA AND CO-DIGESTION OF ANAEROBIC TREATMENT APPLICATION

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By

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RICE STRAW WASHWATER WITH UREA AND CO-DIGESTION OF ANAEROBIC TREATMENT APPLICATION

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Rice straw is a sustainable warranted biomass resource for the production of renewable energy through combustion; and rice straw washing is a simple method to improve the thermal behaviour of straw prior to combustion. Nonetheless, the environmental issue will arise with regards to the produced rice straw washwater (RSWW) if it left untreated, due to the presence of considerable amount of organic matter and leached alkali metals cations primarily potassium. The application of anaerobic biodegradation not only can treat the RSWW but also produce the methane as a fuel. This liquid type substrate is suitable for upflow anaerobic sludge blanket reactor (UASB), where a clear effluent can be produced. This study was conducted in a continuous mode of hydraulic retention time (HRT) 24 hours at mesophilic temperature of 37±2°C. Results indicate the potential of RSWW in generating biogas at organic loading rate (OLR) of 1.0 g COD/L/day, with the stabilized specific methane production (SMP) of 0.16 to 0.18 L CH_4/g COD_{rem} and COD removal between 81% and 83%. However, SMP drop to the lowest production at 0.09 L CH_4/g COD_{rem} as OLR was further increased to 2 g COD/L/day. Continuous accumulation of potassium (K) in the digester, up to 8.0 mg K per gram sludge inoculum correspond to the rapid drop in COD removal along with SMP. The accumulation of K was confirmed and proven by scanning electron microscope (SEM) together with EDX analysis on the inoculum. Addition of 3% urea into RSWW at high OLR enhance the production of methane with the highest average value of 0.21 L CH_4/g COD_{rem}, with the increment by 90.9% compared to RSWW without urea. Meanwhile, during the co-digestion of RSWW and domestic wastewater (DW), the maximum SMP and COD removal were recorded at 0.30 L CH_4/g COD_{rem} and 92.2% respectively, at mixing ratio of 3:7 (RSWW:DW), corresponded to 30.4 C:N ratio. The maintain of TAN below 200 mg/L, pH between 6.5 and 7.0 and IA/PA under 0.3 suggests that the co-digestion of RSWW with DW provide a better stability and higher buffering capacity at high organic loading system without adversely affect the reactor performances. Continuous stir tank reactor (CSTR) showed a slightly better performance in mono anaerobic digestion of RSWW for both COD removal and SMP by 5.1% and 36.4% higher compared to UASB reactor. Nevertheless, the energy balance calculation demonstrated that the net energy output from UASB was 44.4% higher than in CSTR, at 0.26 kWh/kg. This study implies

that the RSWW can be used as a source for renewable energy production and further enhanced by the addition of urea as an external source of nitrogen. Meanwhile, co-digestion is proven to significantly improve the yield of methane along with the removal of organic matter.

Abstrak tesis yang dikemukakan kepada Senat of Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

APLIKASI RAWATAN ANAEROBIK UNTUK AIR BASUH JERAMI PADI DENGAN UREA DAN PENCERNAAN SECARA BERSAMA

Oleh

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Jerami padi adalah sumber biomas yang berkelanjutan bagi penghasilan tenaga yang boleh diperbaharui melalui pembakaran, dan membasuh jerami adalah kaedah mudah untuk meningkatkan kualiti jerami sebelum pembakaran. Walau bagaimanapun, isu alam sekitar akan timbul berkaitan dengan air jerami (RSWW) yang dihasilkan jika ianya tidak dirawat, kerana terdapat banyak bahan organik dan kation logam alkali terlarut terutamanya kalium. Penggunaan biodegradasi anaerobik bukan sahaja dapat merawat RSWW tetapi juga menghasilkan metana sebagai bahan bakar. Substrat jenis cecair ini sesuai untuk reaktor anaerobik aliran ke atas menggunakan lapisan lumpur (UASB), di mana efluen yang jernih dapat dihasilkan. Kajian ini dijalankan dalam mod berterusan pada tempoh tahanan hidraulik (HRT) 24 jam dan suhu mesophilic 37±2℃. Keputusan menunjukkan potensi RSWW dalam menghasilkan biogas pada kadar pemuatan organik (OLR) sebanyak 1.0 g COD/L/hari, dengan penghasilan spesifik metana (SMP) pada 0.16 hingga 0.18 $LCH_4/gCOD_{rem}$ dan penyingkiran COD di antara 81% dan 83%. Walau bagaimanapun, SMP turun ke pengeluaran paling rendah pada 0.09 L CH_4/g COD_{rem} apabila OLR terus meningkat kepada 2 gCOD/L/hari. Pengumpulan berterusan kalium (K) di dalam reactor sehingga 8.0 mg K/g inokulum enapcemar, selari dengan pengurangan pesat dalam penyingkiran COD dan pengeluaran metana. Pengumpulan K telah disahkan dan terbukti dengan mikroskop elektron imbasan (SEM) bersama-sama dengan analisis EDX pada inokulum. Penambahan 3% urea ke dalam RSWW pada OLR yang tinggi, telah meningkatkan pengeluaran metana dengan nilai purata tertinggi 0.21 L CH_4/g COD_{rem}, dengan kenaikan 90.9% berbanding RSWW tanpa urea. Sementara itu, semasa pencernaan bersama RSWW dan air kumbahan domestik (DW), maksimum hasil spesifik metana dan penyingkiran COD masing-masing dicatatkan pada 0.30 LCH_4/g COD_{rem} dan 92.2%, pada nisbah pencampuran 3: 7 (RSWW:DW) bersamaan dengan nisbah C:N pada 30.4. Penyelenggaraan TAN di bawah 200 mg/L, pH antara 6.5 dan 7.0 dan IA/PA di bawah 0.3 menunjukkan bahawa pencernaan bersama RSWW dengan DW memberikan kestabilan yang lebih baik dan kapasiti penyerapan yang lebih tinggi di dalam sistem pemuatan organik yang tinggi tanpa menjejaskan prestasi reaktor. Reaktor tangki teraduk selanjar (CSTR) menunjukkan prestasi yang lebih baik untuk pencernaan mono anaerobic bagi RSWW dalam penyingkiran COD dan SMP sebanyak 5.1% dan 36.4% lebih tinggi berbanding dengan reaktor UASB. Walau bagaimanapun, pengiraan keseimbangan tenaga menunjukkan hasil tenaga bersih dari UASB adalah 44.4% lebih tinggi daripada CSTR, pada 0.26 kWh/kg. Kajian ini menunjukkan bahawa RSWW boleh digunakan sebagai sumber untuk penghasilan tenaga yang diperbaharui dan boleh dipertingkatkan lagi dengan penambahan urea sebagai sumber luar nitrogen. Sementara itu, pencernaan bersama terbukti secara signifikan meningkatkan penyingkiran bahan organik bersama dengan hasil metana.

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Thank you.

I certify that a Thesis Examination Committee has met on 6 June 2018 to conduct the final examination of Nurul Shafiqah Rosli on her thesis entitled "Rice Straw Washwater with Urea and Co-Digestion of Anaerobic Treatment Application" in accordance with the Universities and University Colleges 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 Master of Science.

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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 Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

AD	Anaerobic digestion
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CH_4	Methane
CSTR	Continuous stirred tank reactor
DW	Domestic wastewater
EDX	Energy-dispersive x-ray
HRT	Hydraulic retention time
IA	Intermediate alkalinity
K	Potassium
N_2	Nitrogen gas
OLR	Organic loading rate
P	Phosphorus
PA	Partial alkalinity
RSWW	Rice straw washwater
SBP	Specific biogas production
SEM	Scanning electron microscopy
SMP	Specific methane production
SW	Synthetic wastewater
TA	Total alkalinity
TAN	Total Ammonia nitrogen
TN	Total nitrogen
TS	Total solids
UASB	Upflow anaerobic sludge blanket

CHAPTER 1

INTRODUCTION

1.1. Background of Study

The global energy demand is continue to increase; mainly due to the rapid industrial growth along with growing and expanding of the population (Lim et al., 2012). The long-term prognostications stipulate that the demand for the energy will keep on growing rapidly. This eventually raises the worldwide concern on how to satisfy the future energy demand (Islam et al., 2014) and presently, this demand is mostly fulfilled by utilizing the fossil fuels as a primary energy source (Weiland, 2010). In Malaysia, the major source for power generation was coming from fossil fuel utilization which mainly from coal and natural gas, depicted in Figure 1.1. Conversely, the large-scale use of fossil fuels will not only result in a continuous depletion of existing fossil fuel reserves, but also will adversely affect the environment due to the greenhouse gases (GHGs) emission mainly carbon dioxide which leads to a global warming impact (Barbir et al., 1990; Shafiee and Topal, 2009).

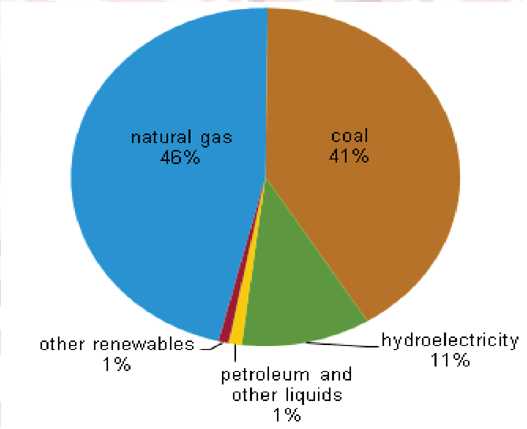

Figure 1.1: Source of Malaysia's Electric Generation in Year 2015 (EIA, 2017)

Recently, the researchers from the Intergovernmental Panel on Climate Change (IPCC) have done the research on global warming and anticipated that in year 2100, the average world temperature could escalate between 1.4 and 5.8°C. This will eventually result in the melting of the polar ice cap thus cause in the global rise of sea levels, the frequent occurrence of the natural disaster and the aggravation of extreme climate phenomenon for instance storms, floods, droughts, related landslides and wildfires (Nakicenovic et al., 2000). In his blog, Datuk Seri Najib Tun Razak the Malaysia Prime Minister said that, the effects of global warming are real and Malaysians could feel it where the drought and rainy seasons were prolonged, occurrences of water resource crises at some places, in addition to the worst floods the nation has faced in decades. In addition, when it came to carbon dioxide emission from the fuel combustion, Malaysia ranked 26th worldwide in the year 2016. Thus, in 11th Malaysia plan (2016-2020), several policies were carried out aimed to reduce Malaysia's carbon footprint by preserving the natural resource, adopting the sustainable consumption and production along with pursuing the green evolution environment (Bernama, 2015).

1.2. Rice Straw Production in Malaysia

Malaysia is known as one of the leading producers of paddy. Due to the emerging of technological development in the agricultural industry, the paddy production target has been increased by 30% and expected to yield about 6.58 million tonne annually by the year 2020 (Shafie, 2015a). Recently the new interest has risen on paddy and rice industry between the agronomy policymakers, as the government has mandated the Ministry of Agricultural and Agro-based Industry (MOA) to administer this industry (Harun & Engku Ariff, 2017). In the year 2015, 730 thousand hectares area was planted with paddy, indicating the increment by 7% compared to 679.2 thousand hectares recorded in the previous year with the corresponding increase in the paddy yield by 473.0 thousand tonnes (16.6%) (Shafiea et al., 2013). The consistent increased of plantation area for paddy and the yield of paddy per metric tonnes every year was due to the growing of rice demand which parallel to the population growth.

It was estimated that about 1-1.5 kg of rice straw will be generated for each kg of paddy harvest (Urmila et al., 2012). In Malaysia, annually about 3.18 million tonne of rice straw will be produced and it was forecasted that the values will be increased year by year towards 2020 due to the emerging technology development in the agricultural industries (Shafie, 2015b). Parallel to this, the paddy residue will also increase, which leads to the problem regarding the paddy waste management. In Malaysia, currently the abundant annual production of rice straw which could be regarded as a potential energy value are still unexploited where the straw is disposed through an open field burning, and thus threatening the quality of environment (Lim et al., 2012; Hosseini and Wahid, 2014; Rosmiza et al., 2014)

Therefore, an agricultural waste biomass specifically rice straw can become the alternative source of energy, hence reducing the greenhouse gases emission by replacing the fossil energy besides avoiding the open burning which leads to local pollution issues. Among the available techniques, direct combustion of rice straw offers an advantage due to its higher energy conversion efficiency than those of others such as anaerobic digestion, gasification, pyrolysis, and thermochemical digestion. Generating electricity and heat by straw combustion not only can preserve the environment, reduces the field-burning pollution and save the energy but also will increase the financial gain of farmers (Said et al. 2013). It was reported by Shafie et al. (2014) that the potential generation of energy from paddy residue is 5652.4 GWh, which represent about 5.4% of total energy demand in Malaysia.

1.3. Problem Statement

Nevertheless, the direct combustion on rice straw displays several technical limitations affecting the systems of thermal conversion. The issue comprises the corrosion problems, slag formation, fouling, sintering and high ash content. To address this issue, rice straw leaching/washing with water can be utilized because it can easily reduce the content of unwanted compounds (ash contents such as potassium and chlorine) that causing fouling and slag formation (Bakker et al., 2013; Said et al., 2013). Jensen et al. (1997) reported that pretreatment methods, such as straw washing can enhance the straw quality because leaching allow the rapid potassium removal considering that it is unrelated to plant constructional components (Idrus et al., 2012).

Even though the thermal behavior of rice straw for combustion can be enhanced through straw washing but, the washwater produced from the washing contains the washed organic matter in substantial amount, which require treatment prior to disposal (Idrus et al., 2012). Moreover, as alkali metal cation (or known as salt) mainly potassium (K) can easily be leached out during the rice straw washing, thus its presence at high concentration is contributing to the salinity in RSWW. Until today, no study has been addressed on the produced washwater either for its further application or treatment. The enhanced anaerobic digestion where a clean renewable energy (biogas) can be generated from the organic waste may be a promising approach for the treatment of rice straw washwater (RSWW), at once could also become the potential source for the green energy production. Aside of its advantages in low operating cost and sludge production, the produced methane could have several applications such as, heat and electricity generation, vehicle fuels and production of chemicals.

Several studies have been conducted using rice straws as mono substrates for batch biogas production. Aside of long hydraulic retention time required, the main challenges are high carbon-to-nitrogen content and very low biodegradability. Nonetheless, no study has been conducted on the continuous anaerobic digestion of RSWW, where a short hydraulic retention time can be applied due to no direct dealing with the lignocellulosic characteristic of rice straws. In addition, even though several studies have been conducted on the treatment of highly saline wastewater by anaerobic digestion application which mainly focussing on the toxic effect of sodium, but little attention were given on the effect of continuous feeding of high potassium concentration, salt which is most likely contributed to RSWW salinity.

In this study, the application of anaerobic digestion treatment, could evaluate the potential production of methane from the rice straw washwater (RSWW), at once proposed a fully utilization of rice straw as a source of renewable energy. To date, no study has investigated the potential of biogas production from anaerobic digestion of RSWW. Therefore, this study aims to assess the potential generation of biogas from RSWW by investigating its biodegradability rate in relation to specific methane production at increasing organic loading rate. The synergistic or antagonistic effect and salt inhibition were evaluated during the continuous digestion of RSWW at high organic loading. Additionally, several approaches to improve the potential of RSWW for a greater biogas production were studied.

1.4. Aim and Objectives

The main objective of this study is, to investigate the potential production of methane from organic rice straw washwater (RSWW) as a source of biomass for anaerobic digestion purposes, thus improve its production by two different approaches. The objectives are divided into sub-objective as follow:

1) To assess the biodegradability rate of RSWW at increasing organic loading rate and investigate the effect on the anaerobic digestion performance at high organic loading of RSWW in relation to K accumulation.

2) To evaluate the effect of urea addition at various concentration on the specific methane production in high organic loading of RSWW.

3) To determine the result of productivity in specific methane during the co-digestion of RSWW and domestic wastewater.

4) To compare the performance of UASB reactor with continuous stirred tank reactor (CSTR) for mono anaerobic digestion of RSWW at constant operating condition (e.g.: temperature and organic loading rate).

1.5. Scope of Study

This study is focusing on the anaerobic digestion of RSWW and its potential for biogas production by using UASB reactor. The biodegradability of RSWW will be studied by investigating the effect of the gradual increment of OLR in term of specific methane production as well as COD removal efficiency. The salinity effect of RSWW at high organic loading will also be assessed in terms of its accumulation in the digester towards the specific methane yield and the COD removal efficiency. Furthermore, the two different approaches to improve the biogas yield were covered in this study. The effect of the addition of urea on RSWW and the potential of co-digestion of RSWW with DW were investigated in order to see if there was any synergistic effect between the two wastes in enhancing the methane yield throughout the process. Last but not least, the continuous stirred tank reactor or known as CSTR will be employed at the same operation condition as UASB reactor was, to compare the performance of both digesters for the anaerobic digestion process of RSWW.

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