

Assessment of potential biogas production from rice straw leachate in upflow anaerobic sludge blanket reactor (UASB)

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Abstract

This study evaluates the potential of Rice Straw Leachate (RSL) to generate biogas and investigate its biodegradability by determining the differences between the theoretical yield and the actual one at its increasing organic loading rate. Seven litre working volume of Up-Flow Anaerobic Sludge Blanket (UASB) reactor is employed under mesophilic condition at temperature of 38 for approximately 17 consecutive weeks. The process performance was evaluated based on the efficiency of COD removal and Specific Methane Production (SMP) in relation to the other parameters such as pH, Organic Loading Rate (OLR), Total Ammonia Nitrogen (TAN) and alkalinity ratio. The OLR were varied at 0.43, 0.55, 0.9 and 1.55g COD/L/d with average COD removal of 79%, 81.2%, 76.1%, and 75.8% respectively. The stability of anaerobic digestion of RSL in UASB was found maintained at an increasing OLR with indicator of pH, TAN and IA/PA ratio that always maintain in the range of 6.5-6.8, below 200mg/L and 0.3 respectively. Meanwhile, the optimum average SMP and COD removal efficiency were 0.18L CH₄g⁻¹COD_{rem} and 81.2% respectively, at applied OLR of 0.55g COD/L/d. This study also revealed a relatively high deviation of SMP from its theoretical value, indicating its low degradability and the limitation of nutrient factors present in RSL.

Keyword: Anaerobic digestion, chemical oxygen demand, rice straw leachate, specific methane production

1. Introduction

The growing of population and rapid industrial development are the main contributors for the increasing trend in global energy demand [1], and currently, about 88% of this demand is met by fossil fuels utilization [2]. However, concerning the issues related to the continuous exhaustion of existing fossil fuel reserves, the rising cost for crude oil, as well as the global warming impact (a result of fossil fuels combustion), many researchers all over the world have an urges to find the alternative of fossil fuels which is suitable, feasible, economic, sustainable and environmental friendly [3]. In this context, biogas (mixture of methane and carbon dioxide) in the form of renewable energy, produced by Anaerobic Digestion (AD) of organic matters can become a great replacement for fossil fuels thus hold an important role in the future [2].

Among the numbers of existing biomass resources available to produce biogas (such as, agricultural crops and residues, industrial wastes, municipal solid waste, and sewage waste), municipal sludge from waste-water treatment plants is currently the main source used [4]. Nevertheless, recently the abundance amount of agricultural residue produced, such as rice straw with global production of about 731 million tons annually, has become an important subject as a source of fuel for energy generation [1], [5], as improperly managed such organic wastes the same as wasting a potential energy value at once threatening the environmental quality. Currently, an open-field burning is one of the most common practice of handling rice straw by the farmers after the harvesting period in many countries in Asia including Malaysia [1], [6], [7], due to its feasible process, inexpensive and there are no markets for straw [8]. However, this activity can give a bad health effect towards children and patients with asthma particularly, as particles produced by the rice straw burning can easily invade the lungs causing a respiratory disease.

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Moreover, rice straw burning can result a severe environmental pollution such as air pollution as well as the increase of greenhouse gases (GHG) (CO_2 , CH_4 , SO_2 and nitrogen oxide) emission, which has been identified to be the main causes of global warming over the last 50 years [9]-[11].

Besides that, some other conventional disposal options such as incorporated the straw with soil is also not recommendable as it will cause the reducing of crop yields due to degradation of soil condition and the increased of foliar disease [12], at the same time generates between 2.5 and 4.5 times more methane than burning the straw [8], [13], [14]. Thus, AD can become one of the promising sustainable alternatives for the disposal management of rice straw due to the production of renewable energy (biogas) as a by-product [11]. GHG could also be reduced from biogas utilization compared to fossil fuels. Apart from biogas production, the mineralized effluent obtained from AD can be utilized as a bio-fertilizer with high concentrations of nitrogen, phosphorus and potassium (NPK) [15]. However, as rice straw is a lignocellulosic material containing cellulose (37.4%), hemi-cellulose (44.9%), lignin (4.9%) and silicon ash (13.1%), it will cause the difficulties during the degradation process as ligno-carbohydrate complexes thus become an obstacle for microbial conversion [16], [17]. Hence, many types of pre-treatment have been undertaken in order to enhance the AD of rice straw such as physical, chemical, biological, pH, temperature and etc. [18] but not all are practical, feasible and typically energy efficient to be applied in industrial sector [17].

Therefore in this study, the organic wash water or known as rice straw leachate (RSL) extracted from the raw rice straw might hold the potential for biogas production with a simple pre-treatment technique. Besides, none of the previous studies have investigated biogas potential from AD of RSL. For that reason, the objective of this paper is to evaluate the potential of RSL to generate biogas and investigate its biodegradability rate by determining the differences between the theoretical methane yield and the actual one at its increasing OLR. AD has been chosen to be the suitable method for the treatment of RSL, as it is associated with a low operational cost, low sludge production, and also the methane produced as the by-product of the process could be used as an energy source for power and heat generation, as well as gaseous vehicle fuel [19], [2].

2. Materials and Methods

2.1. Substrates and inoculum

The rice straw used in the study was collected from paddy field located at Jempol, Negeri Sembilan. It was preselected in order to remove particulate components which include fine stones. Subsequently, the rice straw was dried and cut up into approximately uniform length before it was soaked in tap water. The RSL is produced in a ratio of 18g of dried rice straw to 1 litres of tap water and left for soaking at least for a week.

Table 1. Compositions of synthetic wastewater preparation in 1L volume [20]

Materials	Amount
Yeast (granular form)	23g
Urea	2g
Sugar	11.5g
Full cream milk	144mL
Blood	5.75mL
Tap water	Make up volume until 1L

Meanwhile, synthetic wastewater as explained by Idrus *et al.*, [20] was used as a substrate during acclimation period as it allowed the use of a consistent ingredient of control feedstock with high biodegradability. The materials used for synthetic sewage preparation are shown in Table 1 below. On the other hand, the activated sludge used were originated and collected from wastewater treatment plant at Faculty of Engineering, University Putra Malaysia.

2.2. Analytical methods

The parameters tested in the influent and effluent (treated influent-product from reactor) will allow the determination of the efficiency of the reactor in treating the waste as well as producing the biogas as a renewable energy. During the reactor operation, biogas production were monitored and recorded daily as well as for parameters such as, pH and COD. Meanwhile, total alkalinity and total ammonia nitrogen were determined once per week. The analysis were performed in duplicate in order to ensure the consistency of the readings. All parameters were determined according to standard method for the examination of water and wastewater [21].

Biogas production were monitored and recorded daily using the water displacement method, through water acidified or known as acidified brine solution. Brine solution preparation was referred as method suggesting by Iyagba *et al.*, [22] where NaCl will be added to water until supersaturated solution form. Then, followed by a few drops of H₂SO₄ to acidify the brine solution. On the other hand, for the determination of biogas composition, the analysis was performed using Agilent Technology, 6890N Network Gas Chromatography System.

2.3. Experimental set-up

AD of RSL was conducted using 7L working volume of up-flow anaerobic sludge blanket (UASB). UASB was fabricated using opaque polyvinyl chloride (PVC) sheet solid with the following dimensions: 87 cm internal diameter and 11 cm height with a cylindrical shaped. The reactor set-up as shown in Fig. 1.

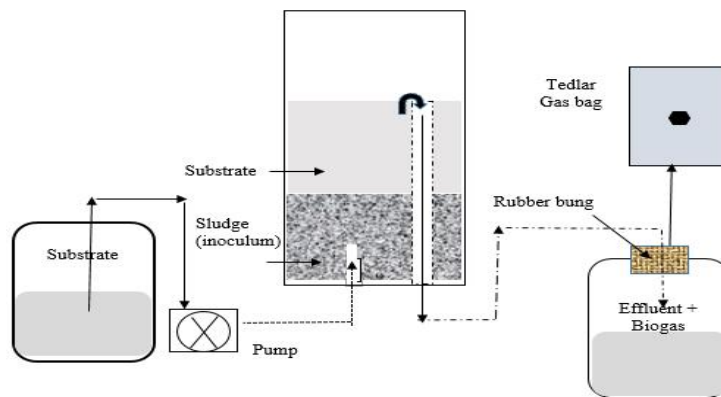


Fig. 1. Experimental UASB set-up.

The reactor has two ports for each influent and effluent at its bottom part. The influent was fed into the digester by a solenoid driven dosing pump. Whereas, the effluent and the produced gas were collected into the sealed effluent container connected with Tedlar gas sampling bag. The UASB is heated by water bath method to mesophilic condition at temperature of 38. For the start-up, the digester was seeded with activated sludge at mesophilic condition. The synthetic wastewater was fed into the reactor on daily basis with OLR of 0.43gCOD/L/day and hydraulic retention time (HRT) of 1 day until the steady state condition was achieved (constant removal of COD) before substituting the feeding with RSL at increasing OLR. Table 2 shows the five phases of AD of RSL performed in this study.

Table 2. UASB reactor operating condition during experimental work

Phase	Days	Feedstock	OLR (g COD/L/d)
I	Acclimation (1-40)	Synthetic wastewater	0.43
II	41-65	RSL	0.43
III	66-93	RSL	0.55
IV	94-118	RSL	0.90
V	119-138	RSL	1.55

3. Result and Discussion

3.1. Characterization of rice straw leachate and synthetic wastewater

Both substrates RSL and synthetic wastewater were analysed immediately after prepared. The characteristics of RSL as stated follows: COD 2200mg/L; Total Nitrogen 48mg/L; pH 6.54; Total alkalinity 571mg/L; K 319mg/L; Na 56mg/L; Zn n.d and Cu n.d. The characteristics of synthetic wastewater are: COD 2200mg/L; Total Nitrogen 80mg/L. Both RSL and synthetic wastewater were stored at 4 to avoid the deterioration of sample

3.2. UASB reactor performance on anaerobic digestion of rice straw leachate

pH

pH is one of the important parameter in biogas production management as indicator for degree of stability. Fig. 2 shows the pH distribution over 138 days of experiments. In general, throughout the experiments, pH of the effluent at all phases were maintained at above 6, with no additional of caustic chemicals for pH adjustment or to maintain process stability. At the beginning of the experiments, where the acclimation phases took place, the synthetic wastewater was fed into the UASB. Graph showed a fluctuation of pH with the minimum and maximum reading of 6.08 and 6.85 respectively, and maintained at 6.65 until the feeding was switched with RSL. The increase of pH to the optimum may be contributed by the lower starting OLR applied which is 0.43g COD/L/d indicating the good start-up or acclimation process in the reactor. Phase II was started at day 41 with RSL feeding at OLR of 0.43g COD/L/d. The declining of pH from 6.67 to 6.56 was observed when the feeding was changed from synthetic wastewater to RSL as the sudden switch of feeding might cause a disturbance in the AD system.

A fast recovery was observed, as on day 43, the pH was back to 6.67 and continuously increased up to 6.85. Throughout the remaining phases (III, IV, V), when the OLR of RSL were increased to 0.55, 0.9 and 1.55 g COD/L/d, pH distribution showed no significant increase or decline and just maintained in the range of 6.6-6.8. According to Ward *et al.*, [23], and Cioabla *et al.*, [24], range pH of 6.8-7.2 was found to be optimal for AD process, and tolerable at a range of 6.5-8.0. Meanwhile, Labatut and Gooch, [25] stated that pH in range 6.5-7.6 are the accepted range of pH for an efficient AD and it is in line with Liu *et al.*, [26] whom stated that the optimum pH range is between 6.5 to 7.5 though the optimal range might be varied depends on the substrates and digestion technique used. Thus, this indicates that the AD of RSL in UASB was stable and well buffered throughout the experiment and able to achieve the steady state condition at the increasing OLR.

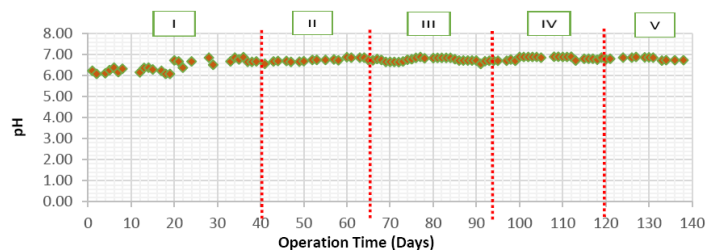


Fig. 2. Distribution of pH.

Ammonia nitrogen and IA/PA ratio

Fig. 3 represents the variation of total ammonia nitrogen (TAN) and alkalinity ratio. Ammonia Nitrogen (AN) is one of the important factors which are known to cause a toxic effects and complete failure of methanogenesis thus towards AD system [27]. According to Franke-Whittle *et al.*, [27] ammonia nitrogen can cause inhibition towards methanogenesis at concentration of 1.7g/L and above. From the graph, generally TAN concentration was seen to be increased as the OLR was increased.

However, there is no significant difference of TAN at phase II and phase III due to small differences of OLR applied. The significant increment of TAN at phase IV and V indicating the increased of nitrogen or protein concentration presented in the RSL as the OLR was increased [28]. Even though there is a significant increase of TAN as OLR was increased up to 1.55g/L, but the value is still below the values which can inhibit the AD process. Instead, at TAN concentration of below than 200mg/L, it is considered as beneficial for the process AD, as ammonia generally is utilized as source of food for methanogens organisms which speeding up for granules activities in the methanogenic phase [29].

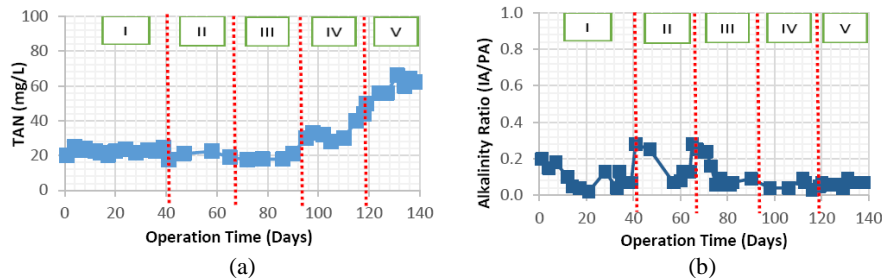


Fig. 3. (a) Ammonia nitrogen distribution. (b) IA/PA ratio distribution.

The proper alkalinity maintenance in UASB reactor is very important to provide the sufficient buffering capacity to withstand the moderate shock loads of volatile fatty acids [25]. Alkalinity can be related to alkalinity ratio, which also known as intermediate alkalinity over partial alkalinity (IA/PA) [30]. Fig. 3(b) shows the IA/PA ratio distribution over 17 consecutive weeks of the experimental work. The value of IA/PA was observed to be always maintained below 0.3 at all phases indicating a good stability of the system during the process of AD of RSL [31]. This is parallel with what has been reported by Ripley *et al.*, [32] and Franco *et al.*, [33] that the ratio between intermediate alkalinity to partial alkalinity must maintain at a value lower than 0.3-0.4 for an adequate performance of AD.

3.3. The removal of COD and specific methane production

In AD, the COD removal can be related with the production of biogas, as the conversion of organic contents into methane. The performance of UASB reactor in the COD removal efficiency, specific biogas production (SBP) and Specific Methane Production (SMP) throughout the experiment are shown in Fig. 4 with the different phases being defined in Table 2. At all phases, a similar pattern of SBP and SMP could be seen. During the first week of phase I, there was a fluctuation and the obvious sudden decrease of COD removal rate indicating the methanogenic microorganism are still adapting themselves towards the applied environment and the incoming organic load which also known as an acclimation period. The subsequent weeks show the steady increment of COD removal with the highest removal rate of 95.6%. Corresponding to COD removal, the SMP also increasing as COD removal increased with the highest methane production of $0.33\text{L CH}_4\text{ g}^{-1}\text{ COD}_{\text{rem}}$. Starting at day 41, the feeding was switched with RSL at the same OLR applied during the acclimation period. It resulted in an immediate decrease of COD removal rate to 77.5% with the corresponding SMP of $0.15\text{L CH}_4\text{ g}^{-1}\text{ COD}$ (Fig. 4). The significant decrease of COD removal rate and SMP could be due to the sudden change of feedstock from synthetic wastewater to RSL. However, after over two consecutive weeks feeding with RSL at OLR of 0.43gCOD/L/d , the removal rate of COD as well as SMP was improved and remain steady at 82% and $0.16\text{L CH}_4\text{ g}^{-1}\text{ COD}$ respectively, indicating a stability of the digester and the achievement of steady state on that specific OLR.

Starting on day 66, the OLR was increased to 0.55gCOD/L/d . The increase of OLR cause a bit changes in the performance, as COD removal rate was observed to decrease to 63% from 82% with SMP of $0.14\text{L CH}_4\text{ g}^{-1}\text{ COD}$. However, it does not take a long time for the reactor to achieve the steady removal rate of COD as the removal remained at 80-84% from day 80 to 93 with the highest SMP of $0.18\text{L CH}_4\text{ g}^{-1}\text{ COD}$. The shorter time required to achieve the steady removal of COD as well as methane

yield were due to the slight differences of OLR applied, whereby the methanogenic microorganism are already acclimatized to that specific range of organic loading. Moreover, the increased of SMP and COD removal rate, could be explained by the stable degradation of the substrate in diluted sample to stabilize the anaerobic degradation [34]. By day 65, the OLR of RSL was increased up to 0.9 gCOD/L/d and the removal rate of COD had fallen significantly to 65.54% together with SMP of 0.09 LCH₄ g⁻¹ COD. The SMP was reduced to about half of maximum yield obtained in the phase III. Despite having a sudden decrease of COD removal rate, it was then recovered by a gradual increase of removal rate and achieved the stable state at day 113 with 78-79% removal rate. The same goes for SMP, the increase up to 0.13 L CH₄ g⁻¹ COD was observed at the end of the day of phase IV.

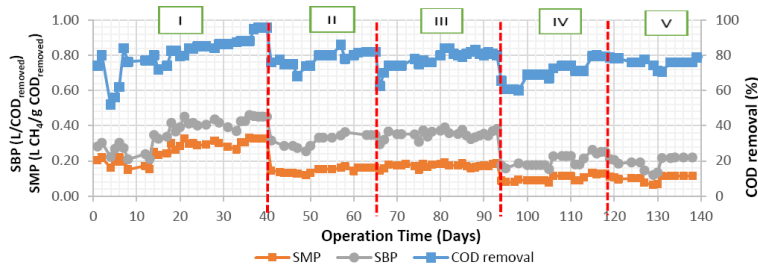


Fig. 4. Distribution of COD removal, specific methane production and specific biogas production at different phases.

Meanwhile, at day 119 the similar trend of COD removal rate were observed when the OLR was raised to 1.55 gCOD/L/d. There is a slight decrease of COD removal rate as well as SMP before the reading recovered and maintained at a steady value. At phase IV and V, the removal rate of COD were found consistent with both phase II and III. In contrast, the SBP and SMP were decreasing as to compare with phases II and III. This could be due to a higher hydrolysis but less methanogenesis, as hydrolytic bacteria are more robust towards environmental condition [35]. To summarize, at the beginning of each phases, the decrease of COD removal rate and SMP were detected and recovered shortly after every OLR change. The increase of OLR from 0.43 to 1.55 gCOD/L/d able to maintain the removal rate of COD from 75-82% indicating the suitable system of the acclimatized UASB for handling RSL at a variable OLR feeding. This would be consistent with the finding by Puyol *et al.*, [36] whom reported that the UASB reactor showed the stable behaviour on AD of cosmetic wastewater after the acclimation period with the average of COD removal efficiency between 78-85%. Moreover, the already acclimatized microbes towards the higher OLR could be explained as to why the stable state removal of COD was achieved in a shorter period of time.

3.4. Biodegradability of rice straw leachate

The performance of biodegradability rate of RSL was studied by calculating the differences between the theoretical with the real production of methane in the experiments. The theoretical SMP in relation to COD as has been reported by Grady *et al.*, [37] is, 0.35m³ CH₄ per kg of COD removed with the production of biogas of about 0.5 m³/kg COD removed. Table 3 presenting the deviation of methane production from its theoretical value at all different phases.

Table 3. Comparison of the SMP for synthetic wastewater and RSL at different OLR

Phase	Average COD removal (%)	Average SMP (L CH ₄ g ⁻¹ COD _{rem})	Theoretical CH ₄ ^a (L CH ₄ g ⁻¹ COD _{rem})	Deviation of CH ₄ ^b (L CH ₄ g ⁻¹ COD _{rem})
I	91.0	0.31	0.34	0.03
II	79.0	0.16	0.28	0.12
III	81.2	0.18	0.28	0.10
IV	76.1	0.11	0.26	0.15
V	75.8	0.10	0.26	0.16

^a calculated assuming 1 g COD = 0.35 L CH₄

^b calculated from the difference between theoretical stoichiometry yield and actual yield per gram of COD removed

Among all phases studied, acclimation with synthetic wastewater shows a higher production of methane with a small deviation from its theoretical value of only $0.05 \text{ L CH}_4 \text{ g}^{-1} \text{COD}_{\text{rem}}$. It was as projected because synthetic wastewater used is known for its high biodegradability [20]. In contrast, by comparing the phases feeding with RSL, the average SMP was found higher at phase III with the applied OLR of 0.55 g COD/L/d . The higher the OLR of RSL, the higher the deviation of volume methane production from its theoretical value, indicating the low degradability of RSL as a substrate. Even though the leachate was fed instead of raw rice straw, but the small portion of rice straw which is lignocellulosic in nature still present as a dross or flakes in a leachate. The higher the organic loading rate of RSL would also increase the presence of lignin and it tended to accumulate and cause difficulties for degradation in AD process [16], [38].

In addition, the low total nitrogen content of RSL could also become the contributor towards the decrement in methane production. According to Dioha *et al.*, [39], the carbon to nitrogen (C:N) ratio of the substrate can greatly affect the biogas production, where the optimum ratio was reported range from 25-35 [17]. In this study, the measured ratio of COD: Total nitrogen is 46:1 indicating the imbalance C:N ratio of RSL. This finding is in line with the previous studies done on raw rice straw, which stated that the untreated rice straw has a very low concentration of total nitrogen which eventually affecting the nutrient balance for the optimum biogas production [16], [40], [17].

3.5. The sludge morphology

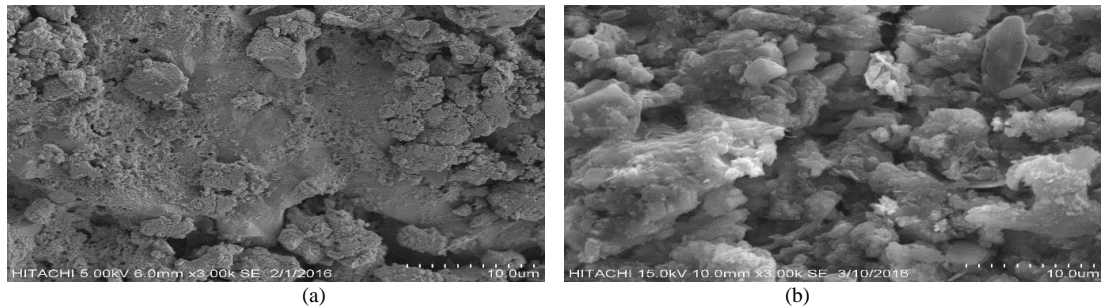


Fig. 5. SEM image of the sludge inoculum (a) before feeding started (b) formation of fine granules after 100 days of operation.

Fig. 5 represent the scanning electron microscope (SEM) image of the inoculum sludge before and after the feeding with RSL. After 100 days of feeding, it can be seen the finer activated sludge has become more compact with the formation of granules. The sludge washout has decreased significantly due to the granulation and result in a good performance of UASB in COD removal rate specifically. The development of sludge granulation is one of the important factors contributed towards the successful operation in UASB [41]. This finding is consistent with the founding by Zhao *et al.*, [42] and Wu *et al.*, [43], whom reported that the pollutants removal efficiency (i.e: COD) was improved by utilizing the granular sludge in wastewater treatment and the size of sludge granule could be proportional with the production of biogas.

4. Conclusions

The process AD of RSL at a variety OLR from 0.43 g COD/L/d to 1.55 g COD/L/d , was able to maintain the stability of a system operated in UASB reactor with indicator of pH, TAN and IA/PA ratio that always maintain in the range of 6.5-6.8, below 200 mg/L and 0.3 respectively. During the feeding of RSL, the highest average of COD removal efficiency found was 81.2% with SMP of $0.18 \text{ L CH}_4 \text{ g}^{-1} \text{COD}_{\text{rem}}$ at OLR 0.55 g COD/L/d . Relatively, the varied OLR of RSL has a substantial influence on biogas as well as methane yield. Nevertheless, a higher organic loading rate could still be applied as the

system did not showed any sign of overloading at 1.55 gCOD/L/d. However, at a higher OLR, the low degradability of RSL content might has a significant effect on the optimum amount of biogas production and resulted in a low methanogenic potential. Generally, the results indicate that, RSL was found to hold the potential for biogas production. However, the imbalance C:N ratio and the low degradability of RSL might cause a restriction towards the optimum production of biogas. The co-digestion of RSL with the other substrates that contain a high degradability properties could be proposed for the optimum production of biogas.

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