EFFECT OF PRE-TREATMENT ON THE ANAEROBIC CO-DIGESTION OF RICE STRAW AND VEGETABLE WASTE FOR BIOGAS PRODUCTION

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Abstract

Co-digestion of rice straw and vegetable waste (represented by green mustard, *Brassica juncea*) was conducted in a laboratory scale experiment for biogas production run in batch mode. Rice straw and *B. juncea* were mixed at certain composition to obtain the C/N ratio of 20 and used as the raw material of the digestion process. Rice straw was subject to biological and physical pre-treatment prior to the digestion. Biological pre-treatment was conducted by mixing the rice straw with EM-4, a commercial enriched microbial source, and physical method of pre-treatment was done by grinding the material. Liquid effluent from an existing biodigester of cow manure was used as inoculums. Digestion process was conducted at mesophilic condition, 35^{o}C. Biogas production was observed daily, whereas concentration of volatile fatty acids (VFA), total solid (TS), and volatile solid (VS) were observed weekly. Following the digestion for about 50 days, the average yields of biogas production were 0.016 L/g VS, 0.030 L/g VS and 0.017 L/g VS, for non pre-treated, biologically pre-treated and physically pre-treated substrates, respectively.

The highest production of biogas was achieved on the day 20 after which the production decreased gradually. The maximum methane concentration in all cases (with and without pre-treatment) was not significantly different. The decrease of pH in all system was observed in the first 15 days and then back gradually to neutral. Slight decrease of pH was again noticed at the end of digestion period, especially in the case of physical pretreated and non pretreated substrates. Residual volatile solid was found to be 33%, 88.5%, and 81.4% of the initial volatile solid for the biologically pretreated, physically pretreated and unpretreated substrates, respectively. Significant increase of biogas production in biological pretreated substrate is mainly attributed to the improvement of rice straw digestibility.

Keywords: Biogas, Co-digestion, Rice straw, Vegetable waste

Introduction

Accumulation of solid waste, shortage of energy source and global climate change are current common issues faced by any society in the world in line with the increase of population. Conversion of waste into energy is believed to be one of the best solution to cope the above issues simultaneously [1, 2]. With more than 250 million populations, Indonesia produces a huge amount of solid waste, especially from household and trading activities, such as traditional markets. It is reported that in 2010 Jakarta the capital city produces more than 9,500 tons of solid waste daily, 67 % of which is compostable waste. Rotten vegetable and fruits and food residues dominate the compostable waste [3]. General characteristics of these wastes are high water content, low pH, and rich in nitrogen. On the other hand, it was reported that about 38-90 million tons of rice straw was produced in 2010, about 70-80% of which is burnt in farming and has not been utilized optimally [4].

Rice straw composes of cellulosic materials and lignin, which are relatively difficult to be degraded resulting significant problems in the operation of biodigesters [5]. Compared with vegetable waste, rice straw contains high carbon and low nitrogen. Thus these two materials, vegetable waste and rice straw, could be used complementary in the production of biogas which requires proportional carbon/nitrogen ratio [6]. Pre-treatment of lignocellulosic material is recommended to accelerate their digestion process in the biodigester [7, 8]. Jin & Chen [9] found that cutting the rice straw into 5-8 cm and then exposed it with steam at various temperatures for 4-5 minutes could enhance its hydrolysis and thus increase the sugar yield. Similar finding was also suggested by Sidiras and Koukios [10]. Biological pretreatment of rice straw using white rod fungi has increased the rate of enzymatic hydrolysis by several folds [11].

This paper presents the results of co-digestion of vegetable waste and pre-treated rice straw in the production of biogas. Both biological and physical were applied and the results were compared. Performance of biodigester was assessed based on the production of biogas, composition of biogas, volatile fatty acids produced during the process and residual substrate.

Experimental

Raw Material

Raw materials used in this study were (a) rice straw which was air dried. This material contained 2.9% of water, 81.63 of volatile solid, 64.68 of C/N ratio, (b) *Brassica juncea* (represented local vegetable waste) containing 10.68% of water, 84.26 % of volatile solid, and 18.44 of C/N ratio. Effluent from existing biodigester of cow manure belongs to KP 4, Recycling Center of Gadjah Mada University, was used as inoculums. Commercial enriched microbial source namely EM4 was used in the biological pretreatment process of the rice straw. EM4 was produced by Songgolangit Persada Company, containing fermentative bacteria from *Lactobaccilus*, fermentative fungi, phosphate bacteria, and yeast.

Sample Preparation

Rice straw was cut into 0.5 cm and divided into 3 parts. The first part was inoculated with EM-4 and incubated in the room temperature for 5 days. The second part was finely grounded. The third part was left as it is without any treatment. Samples J1, J2, and J3 were prepared by mixing 94.5 % of blended *B. juncea* and 5.5 % of biologically pretreated rice straw, untreated rice straw, and grounded rice straw, respectively. These mixtures have C/N ratio of 20 and volatile solid (VS) of 41.98%. Table 1 presents data on the composition and characteristics of each sample.

Table 1. Characteristics of Samples Used in The Study Sample*)

	Composition (mass fraction)				C/N	VS (%)
	Rice Straw	***B. Juncea***	**Water**	**Innoculum**		
J1	0.0275	0.472	0.214	0.285	20	41.98
J2	0.0174	0.481	0.215	0.285	20	41.98
J3	0.0174	0.481	0.215	0.285	20	41.98

*) J1 (biological pre-treatment): size of rice straw: 0.5 cm, added with EM4 (biological starter), J2 (no pre-treatment): size of rice straw: 0.5 cm, J3 (physical pre-treatment): size of rice straw: fine (grounded)

Method of Experiment

Sample J1 was placed in 500 ml erlenmeyer (as biodigester) and was added with innoculum to get the total volume of 350 ml. The initial pH of the sample was measured and then flashed with nitrogen gas to minimize the presence of oxygen. The biodigester was covered with wood stopper having 2 holes (one for placing sampling tube, and the other for gas tube). Gas tube was connected to water manometer to measure the gas produced (see Figure 1). The biodigester was incubated at 35^{o}C by placing in a water bath. Similar treatment was also applied for samples J2 and J3.

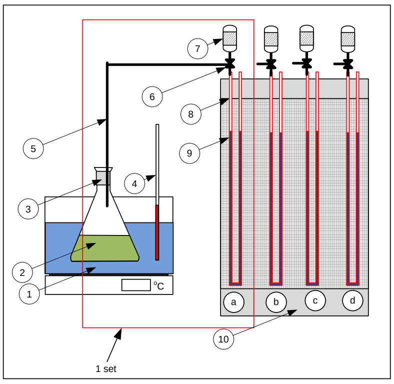

Figure 1. Experimental set-up (1. Water bath, 2. Sample, 3. Sampling tube, 4. Thermometer, 5. Gas tube, 6. Valve, 7. Gas holder, 8. Water manometer, 9. Gas level monitor, 10. Holding board)

During the incubation process, gas produced was monitored daily; its methane concentration was analyzed weekly. Weekly monitoring was also carried out for residual total solid, residual volatile solid, volatile fatty acids, and pH of solution in the digesters.

Production of biogas was measured through the water manometer, whereas the methane concentration was analyzed using Gas Chromatography Shimadzu GC 14B, with SUS Packed Column Porapak Q, FID detector. Total solid and volatile solid were analyzed using gravimetric method. Volatile fatty acids were analyzed using gas chromatography.

Results and Discussions

Biogas Production

Figure 1 shows the accumulated biogas produced during incubation of J1, J2, and J3. It clearly shown that biologically pretreated rice straw gave more than 3 times higher biogas production compared with those with physically pretreated sample. It can also be observed that J2 and J3 gave almost the same volume of gas production. This indicates that physical pretreatment prior to digestion has no significant effect on gas production. It is suggested by Zhang & Zhang [7], grinding of rice straw could have substantial effect on biogas production yield when the method is combined with heating and chemical addition. Methane concentration in biogas produced by all samples does not vary significantly, as shown in Table 2. However, J3 sample gives slightly higher methane concentration, especially at the end period of incubation.

Weekly yield biogas (L/g VS) was calculated based on the removal of volatile solids (VS) and the results are shown in Table 3. Relatively high yield of gas in the early period of incubation demonstrates high production of gas, but the gas contains low methane. This gas is suspected to be the product of internal fermentation of the vegetable [13].

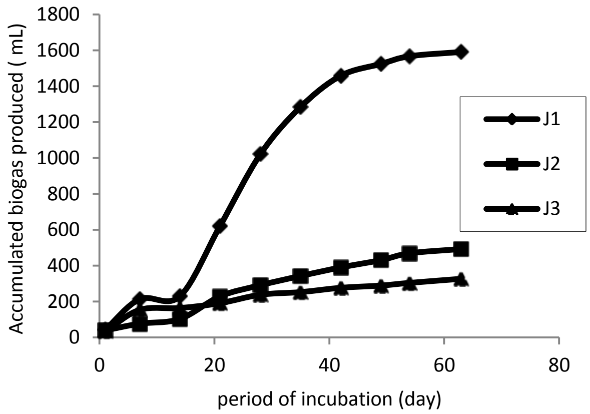

Figure 2. Effect of various pre-treatment of rice straw on accumulated biogas produced from mixture of rice straw and vegetable waste

Table 2. Effect of Various Pre-Treatment of Rice Straw on Methane Concentration

Week	Methane Concentration (%)		
	J1 (Biological Pre-treatment)	**J2 (No Pre-treatment)**	**J3 (Physical Pre-treatment)**
0	0.35	1.20	0
1	16.19	16.45	9.95
2	21.11	43.66	15.78
3	62.48	63.15	38.48
4	63.44	60.74	64.78
5	61.10	55.33	59.81
6	55.72	56.12	58.97
7	54.26	56.53	60.71

Table 3. Effect of Various Pre-Treatment of Rice Straw on Biogas Yield of Rice Straw-Vegetable Waste Mixture

Week	Biogas Yield (L/g VS)		
	J1 (Biological Pre-treatment)	**J2 (No Pre-treatment)**	**J3 (Physical Pre-treatment)**
0	0.029	0.056	0.059
1	0.020	0.015	0.019
2	0.052	0.014	0.016
3	0.037	0.012	0.014
4	0.039	0.009	0.009
5	0.031	0.010	0.009
6	0.030	0.011	0.009
7	0.030	0.016	0.017

Acid Production

Anaerobic digestion of organic materials consists of 4 main steps, each of which is conducted by different microbial consortium, i.e. (i) Hydrolysis of organics is carried out by hydrolytic microorganism producing fatty acids, alcohols and ketones, (ii)

Acidogenesis of hydrolysis products into simpler fatty acids, hydrogen, and carbon dioxide done by acidogenic microorganisms, (iii) Acetogenesis of fatty acids into acetic acid conducted by acetogenic microorganisms, and (iv) Methanogenesis (formation of methane) by methanogenic microorganisms [14]. Thus, analysis of both type and concentration of fatty acids in the liquid samples could reflect the status of each reaction step mentioned previously.

Figure 3 presents the change of pH in the biodigesters and concentration of acetic acid in the solution. As noticed pH for all samples dropped at the early stage, increased gradually, and then levelled off at neutral condition. The decrease of pH is most likely caused by accumulation of fatty acids in the solutions. Once the acids concentrations reduced, the pH started to increase, and at the same time concentration of methane showed gradual increase which indicates the activity of methanogenic microorganisms has been significant (see Figure 4).

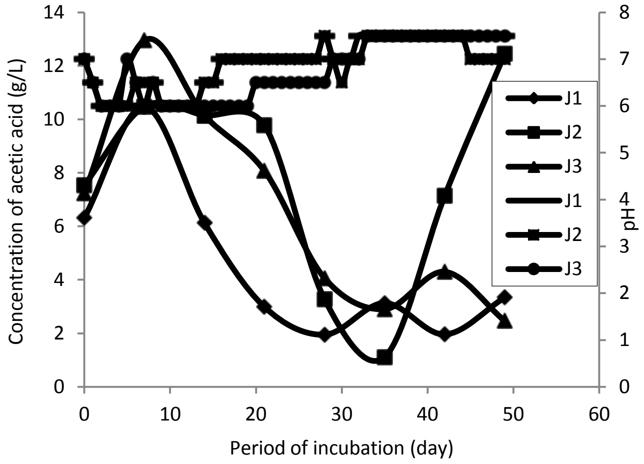

Figure 3. Change of pH and concentration of acetic acid in all samples during the incubation

Accumulation of acids follows similar trend for three samples (J1, J2, J3), especially in the first 35 days of incubation. In the first 5 days, the concentration increased and then decreased sharply up to day 35 (J1 and J3). However, this is not the case of J2 (sample with no treatment). As can be noticed in Figures 3 and 4, acid concentration of J2 increased in the first 5 days, and then stayed constant until day 20, before it finally decreased as J1 and J3. This fact has no substantial effect on methane production. At the end of incubation period, concentration of acid in J2 appears a sharp increase, which is not the case for the other two samples (J1 and J3). Such an increase does not result in the change of methane concentration. Similar pattern was also indicated by concentration of propionic acid of samples J2 and J3 [15]. The reason of this could be due to the delay of organic degradation by acidogenic microorganisms (note that J2 is sample with no pre-treatment and J3 is sample with physical treatment). Different digestibility of different materials could also be another reason [16].

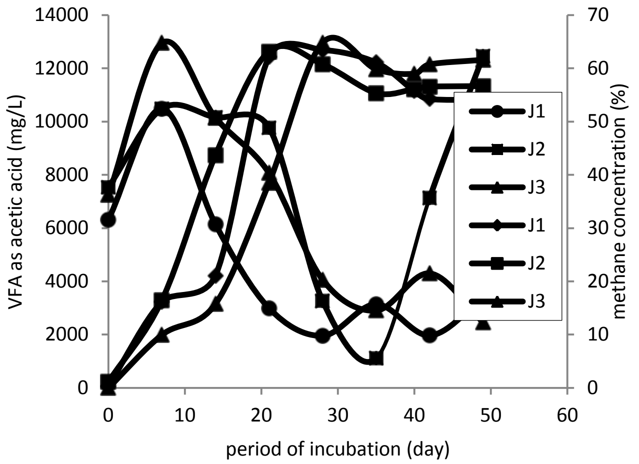

Figure 4. Concentrations of acid in the solution and methane in biogas at various period of incubation for samples with different methods of treatment

Residual Substrates

Residual substrates were analyzed based on the total solid (TS) and volatile solid (VS). The results are presented in Figures 5 and 6. For the period of 56 days incubation, TS and VS of J1, J2 and J3 reduced by 68.4% and 67.1%, 40.3% and 8.8%, 50.8% and 18.6%, respectively. As shown in Figure 5, TS reduction for all samples follows similar rate up to day 50. Then, TS of J1 reduced more significantly compared to the other two samples. Concentration of TS of J1 should have been higher than that of J2 and J3. However, the data presented in Figure 5 shows the opposite results. This could be due to the contribution of biomass in the total solid.

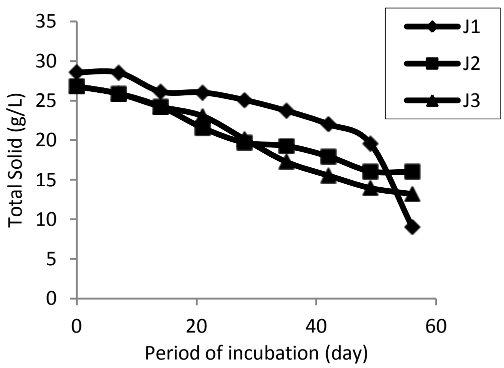

Figure 5. Effect of various pre-treatment of rice straw on the residual total solid

Residual substrate as volatile solid (Figure 6) demonstrates more conclusive results. Sample J1 which is biologically pre-treated sample shows substantial reduction, especially in the second half of incubation period. Again, this indicates that biological pre-treatment is more effective in degrading cellulosic matrix in the rice straw such that anaerobic degradation can proceed more easily. Grinding rice straw (J3) (physical pre-treatment) gives no significant difference on the removal of volatile solid, compared with that of 0.5 cm rice straw (J2), which is also indicated by the quantity of the biogas produced (Figure 2).

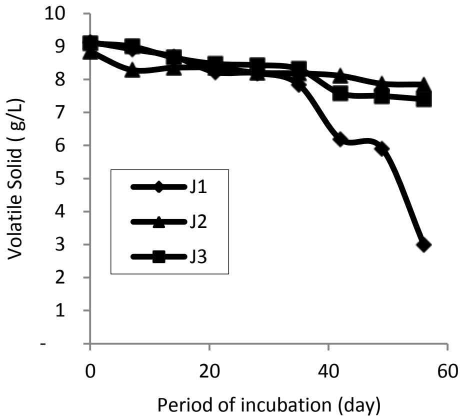

Figure 6. Effect of various pre-treatment of rice straw on the residual volatile solid

Conclusions

Biological pre-treatment of rice straw increases the production of biogas from the mixture of rice straw and vegetable waste by 3 fold, whereas physical pre-treatment gives no significant effect. The biological pre-treatment has also doubled the biogas yield (ml gas/gVS). Maximum concentration of methane in the gas produced is not very much affected by the method of pre-treatment, i.e. about 60%. The biological pre-treatment results in more accessible substrates for conversion to biogas. However, it is not clearly known whether (i) the biological treatment broke the lignocellulosic matrix down into simpler compounds and then the compounds stimulate the activity of anaerobic microorganisms or (ii) those compounds themselves subject to the conversion to biogas, or (iii) combination of (i) and (ii) and/or other mechanisms.

Removal of accumulated VFA in the biologically pretreated sample occurred more significantly compared to that in the physically pretreated sample and sample with no treatment.

The highest rate of biogas production occurred between day 15-20 (during 56 days of incubation), and then it slowed down gradually. Lengthen the incubation period seems no effect on the product obtained although the presence of VS is still relatively high (as in the case of J2 and J3).

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