



Biogas Production through Anaerobic Digestion of Tannery Solid Waste

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ABSTRACT

Annually about 85,000 tons of raw hides and skins are estimated to be processed for leather production in Bangladesh. Tannery generates huge amount of solid and liquid wastes. Anaerobic digestion (AD) is a potential treatment to stabilize waste and produce biogas for renewable energy. The aim of this study was to investigate the potential of AD of tannery solid waste (TSW) generated from the pre-tanning operation and to compare the effect of cow dung as the substrate to TSW. For the reaction with TSW by mixing with different substrates, biogas production was observed starting on 4th day with a steady increase. The cumulative gas production from each of the test reactors operating at the various organic loading of tannery solid waste, domestic sewage, and cow dung were different. This study shows an optimal AD process of TSW by mixing with different substrates for the obtained optimum C/N ratio and also for the high volatile solids (VS). The COD removal rates for the series of 5 reactors (R1, R2, R3, R4 and R5) were 48.75, 50.84, 46.07, 45.94 and 47.78% respectively. Maximum COD removal was achieved from reactor R2 where maximum gas was also produced.

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INTRODUCTION

Leather is one of the most prospective industries in Bangladesh. According to Export Promotion Bureau (EPB) Bangladesh earned \$1.3 billion from the leather sector in the year of 2014-2015, which was the second highest contributor to national exports after garments sector^[1]. A large amount of solid waste is generated daily by leather manufacturing process in this area and untreated disposal of this waste are creating a serious hazard to the environment^[2]. A major portion of the solid wastes from leather industry is fleshing which contains mainly fat, protein and residual chemicals such as lime and sulfide used in the unhairing process of beam house operation^[3]. A huge amount of water is also required during the tanning process. It has been estimated that about 35-40 liters of water is essential in conventional process for every kilogram of leather produced. There are about 113 tanneries in Bangladesh that produce 180 million square feet of hides and skins per year. Most of the tanneries do not have proper treatment plants and generate 20000m³ tannery effluent and 232 tonnes solid waste per day^[4].

Now it is the prerequisite to developing an appropriate waste management system of the tannery waste in a cost-effective and environmental friendly way through appropriate technology. With a rapid depletion of conventional energy sources, the need to find an alternative, preferably the renewable source of energy from waste is becoming increasingly important for the sustainable development of our country.

Bangladesh is in the midst of a severe and worsening energy crisis, with a population of about 160 million living in an area of 147,000 m². It is one of the most densely populated countries in Asia. Around 33% of the total population is covered by electricity network and 4% is covered under natural gas network. About 82% of total electricity comes from natural gas. As the demand is increasing and the reserve of the natural gas is decreasing, it is absolutely obvious to state that Bangladesh is in shortage of natural gas. The continuous depletion of fossil fuel is striking the concern into the search for the new energy source is mandatory. So we should focus our view on the alternative renewable energy sources like solar energy, biogas, biodiesel, wind power, tidal energy etc. Here biogas is one of the promising renewable energy sources in Bangladesh. As

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an agricultural country, Bangladesh has embedded with plenty of biomass which has been used for extracting energy by burning directly or generating biogas.

Biogas typically refers to a gas produced by the biological breakdown of organic matter in the absence of oxygen. It is a flammable gas produced by anaerobic fermentation of organic waste materials. Biogas originates from biogenic material and is a type of biofuel^[5].

Anaerobic digestion (AD) is the conversion of organic material directly to gas, termed biogas, a mixture of mainly methane (CH₄) and carbon dioxide (CO₂) with small quantities of other gases such as hydrogen sulphide (H₂S), ammonia (NH₄), water vapor, hydrogen(H₂), nitrogen (N₂) etc are shown in Figure 1. AD is the process of decomposition of organic matter by a microbial consortium in an oxygen-free environment ^[6-12]. Waste from the leather industry, known as limed leather fleshing, has a low C/N ratio (3-5) and alkaline pH (10-11.5). This is a major disadvantage for anaerobic digestion due to ammonia toxicity for methanogenesis^[13]. Research work for the generation of biogas from tannery solid waste in Bangladesh is yet to be done although the substrate has good potential for biogas generation.

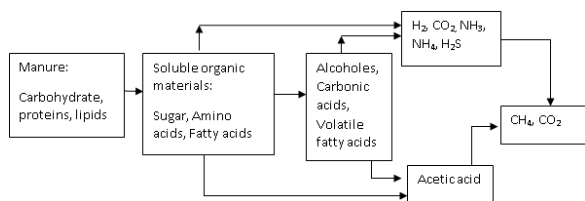


Figure 1. Schematic diagram of anaerobic digestion

MATERIAL AND METHODS

Sample collection

Different types of tannery solid waste were collected from local tannery at the different time in Hazaribagh. Before analysis and other experiments, substrates were collected at different time and stored at 4°C. Through appropriate sampling unit and the characteristics of the waste, the fleshing portion of tannery solid waste was chosen as a suitable substrate for biogas generation^[15].

Preparation of substrates

The limed fleshing used as substrate was grounded to less than 6 mm diameter using a meat-grinding machine. While the domestic sewage and cow dung were collected from different locations of Dhanmondi area. Domestic sewage also acts as a source of various microorganisms required for anaerobic digestion, whereas, cow dung was also used in different proportion as a substrate to maintain the C/N ratio. Sewage and cow dung were also characterized by Standard Methods^[15].

Inoculum

Domestic sewage and cow dung was used as active material for inoculation. The inoculum was prepared in the laboratory using limed fleshing, domestic sewage and cow dung in equal proportions.

Experimental setup

In order to examine the management of solid waste from tanning industry, a simple methanogenic activity test procedure was adopted^[16]. Through the appropriate technology anaerobic digestion was carried out in batch experiments using a 2 L capacity glass bottle. The composition of limed fleshing, domestic sewage, cow dung and inoculum used in the batch experiments are described in Table 1. Table 2 shows that different quantities of waste materials were mixed and added to the glass bottle to obtain an initial volume of 1 L in all the reactors, R1 to R5. The total gas production was measured using a water displacement method at an interval of 24 hours. Temperature and pH probes were installed for daily monitoring. The first outlet was for substrate sampling and the second outlet was for the gas container. Routine anaerobic process indicators were used including pH, COD removal, VS degradation, volatile fatty acid (VFA) concentration, gas production, and gas composition.

Analysis

Carbon and nitrogen contents of the fleshing, domestic sewage were determined by C-H-N elemental analyzer with TCD detector^[17]. Helium gas was used as carrier gas at 250 kPa and 140 mL/min, furnace and oven temperature were 900°C and 65°C, respectively. Moisture and ash contents were measured by gravimetric methods by drying at 105°C and by completing combustion at 800°C, respectively. The protein content was estimated from the nitrogen content multiplying by factor of 6.25. Total solids (TS), VS, and VFA were determined according to the procedures recommended in the standard methods for the examination of water and wastewater^[15]. Assay bottles were analyzed periodically for the above-mentioned parameters for a period of 8 weeks. Gas production from the reactors was monitored by means of water displacement method on daily basis. The volume of water displaced from the bottle was equivalent to the volume of gas generated at the temperature and pressure that prevailed during the study period. Gas chromatograph with TCD detector was used to measure methane content and carbon dioxide in the biogas composition^[18]. Helium gas was used as carrier gas at 900 kPa and 10.5 mL/min, oven and detector temperature were 80°C and 180°C, respectively.

Experimental procedures and sampling schedules

A known quantity of wastes was added in a 2 L bottle as an initial experiment. On the basis of the result of the experiment, five biogas digesters were taken for biogas

TABLE 1. Characteristics of substrates

| Constituents | Limed Fleshing | Domestic Sewage | Cow dung | Inoculum |
|-------------------------|----------------|-----------------|----------|----------|
| pH | 8.4 | 6.50 | 6.67 | 6.78 |
| TS (%) | 11.57 | 4.0 | 15.0 | 6.0 |
| VS (%) | 81.32 | 80.0 | 86.0 | 85.70 |
| Oil (%) | 7.4 | 2.15 | 1.36 | - |
| Protein (%) | 42.53 | 21.61 | 7.35 | - |
| Moisture content (%) | 88.45 | 96.0 | 85.0 | 95.0 |
| COD (mg/L) | - | 1490 | - | - |
| Calorific Value (MJ/kg) | 19.156 | 17.842 | 21.564 | - |
| C/N ratio | 2.51 | 18 | 21.0 | - |

TABLE 2. Quality of lime fleshing, domestic sewage, cow dung and inoculums and the initial VS concentration in the reactors

| Reactors Name | Fleshing (g) | Domestic Sewage (mL) | Cow dung (g) | Inoculum (mL) | Tap water (mL) | Initial VS concentration (g/L) |
|---------------|--------------|----------------------|--------------|---------------|----------------|--------------------------------|
| R1 | 145.00 | 350.00 | 200.00 | 100.00 | 320.00 | 52.86 |
| R2 | 190.00 | 500.00 | 110.00 | 100.00 | 200.00 | 50.41 |
| R3 | 250.00 | 650.00 | 0.00 | 100.00 | 90.00 | 55.65 |
| R4 | 210.00 | 550.00 | 60.00 | 100.00 | 150.00 | 53.78 |
| R5 | 300.00 | 700.00 | 150.00 | 100.00 | 270.00 | 56.45 |

generation from the substrate by mixing with domestic sewage in different proportions. The digested slurry from the initial experiment was used as inoculum for the test reactors. Thus, the test reactors for five different organic loading were constructed. The TS concentration of all reactors was 6%. At the end of every week, one bottle for each VS load was analyzed for various parameters.

RESULTS AND DISCUSSION

Characteristics of raw materials

The fleshing contains 81.32 % VS which was considerable amount (9.50%, dry basis). It also contains protein of about 42.53%. The C/N ratio of fleshing was 2.51, which were quite low for optimum biogas generation; then the low C/N ratio was increased by mixing with cow dung and domestic sewage. The pH of the fleshing was very high (8.4), which are not favorable to biogas generation. Buffering capacity of cow dung was high and the domestic sewage would also act as a source of various microorganisms required for the anaerobic digestion.

Biogas generation

Daily gas production

Figures 2 to 6 represent the volume of daily gas accumulated with varying amount of fleshing. For substrate fleshing, sewage sludge and cow dung were used. In the mixture, initially few days were required for biogas generation. After 5 days, biogas generation started properly and then gas generation per day was in increasing trends. Then after 45 days, food concentration of bacteria decreased and biogas generation was also significantly decreased. Due to changes in temperature, the gas production was irregular and for scum formation on the surfaces of the slurry of the biogas digester was

also uneven. So, after breaking of scum by the pressure of the biogas inside the digester, sometimes the amount of biogas abnormally increased.

Figure 2 shows the daily gas generation for reactor R1. It was observed that gas generation started at the very next day of charging the digesters with the slurry. The rate of gas generation gradually increased with increasing the digestion period. The data also indicates that during the digestion period, most of the day gas production range was in between 300-600 mL. In this reactor, the peak gas production of 1120 mL was observed on the 31st day. It was observed that gas production rate declined after 53rd days.

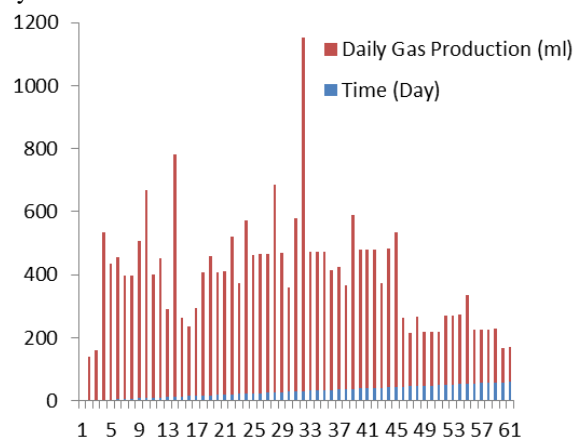
**Figure 2.** Daily gas production in the reactor R1

Figure 3 shows the considerable amount of daily gas generation in reactor R2. In this reactor also the generation of gas started from the second day after recharging the reactor with slurry. The peak gas production was observed on the 25th day, the amount was 1130 mL. Here also the gas production range was in between 150-600 mL. Figure 4 represents the daily gas

production rate for reactor R3. This shows the lower range of daily gas production (100-600 mL). In this digester, bacteria were taken four days for acclimatization as there was no cow dung in the slurry. The peak gas production was observed 580 mL at the 20th day of digestion period. Figure 5 depicts the generation of gas starts at the second day after charging the reactor R4. The peak gas was 570 mL which were observed at the 17th day. The gas generation also ceased on the 60th day of digestion period. Figure 6 illustrates the daily gas production in the reactor R5. In this reactor the peak gas production 600mL which was observed at the 20th day. A gradual shift was observed in the period of peak gas production with increasing VS concentration.

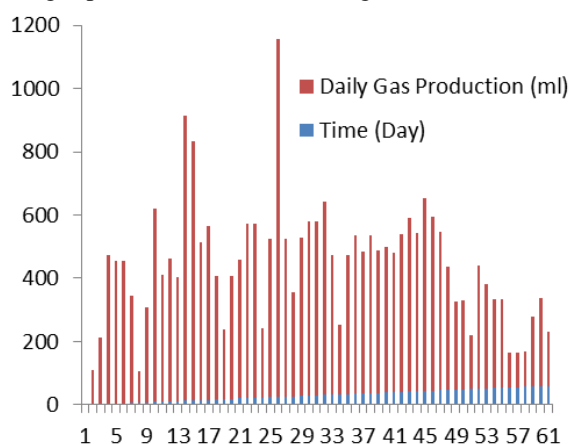


Figure 3. Daily gas production in the reactor R2

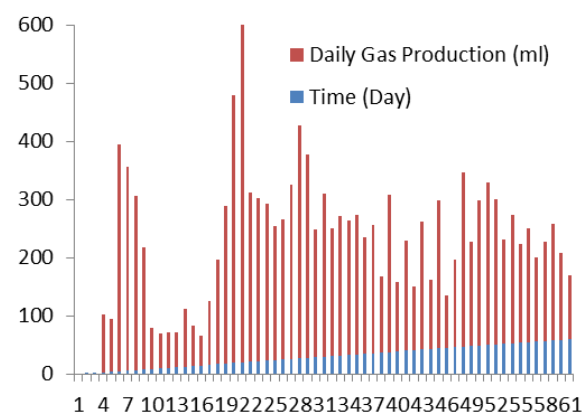


Figure 4. Daily gas production in the reactor R3

Comparison of different reactors daily gas production (mL)

A promising achievement is predicted with the produced optimum condition and appropriate technology. Figure 7 represents the comparison of five reactors daily gas production in mL.

Cumulative gas production

The cumulative gas production from each of the test reactors operating at the various organic loading of

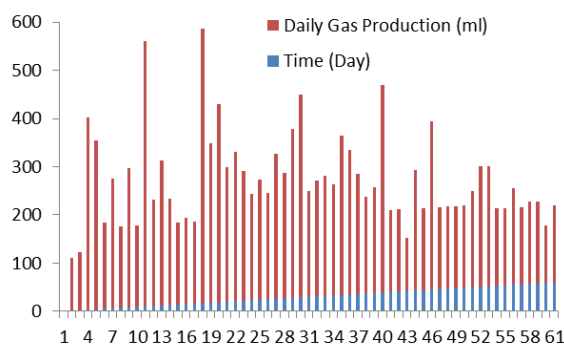


Figure 5. Daily gas production in the reactor R4

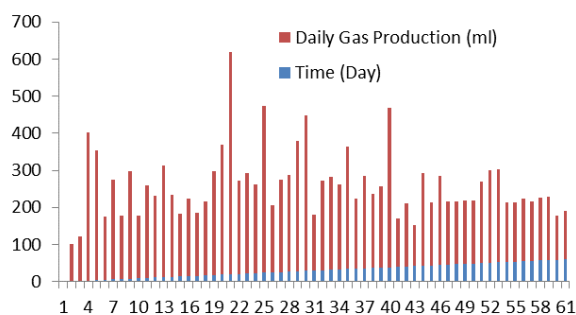


Figure 6. Daily gas production in the reactor R5

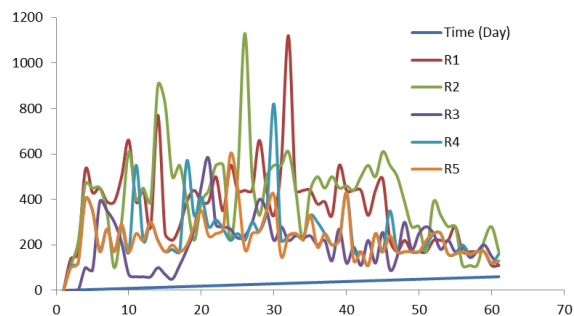


Figure 7. Comparison of daily gas production (mL) from five reactors

tannery solid waste, domestic sewage, and cow dung are shown Figure 8. A cumulative gas production from test reactor R1 was 22,220mL at the end of the eighth week of the study period. A cumulative gas production from the test reactor R2 was 25,030 mL, while a cumulative gas production of 12,170 mL was observed in test reactor R3. In the fourth reactor R4 cumulative gas production was observed 14,850 mL and the reactor R5 cumulative gas production was observed 13330. In the five reactors, R1, R2, R3, R4, and R5 specific gas production in terms of VS fed were 0.4321, 0.457, 0.217, 0.259 and 0.350 L/g, respectively. Figure 8 shows that the lag phase prevailed upto 5 to 6 days of digestion period. This was due to microbe limiting at the initial stage of the fermentation.

The peak generation of gas is delayed as the lag phase was longer. After the lag period, the cumulative volume of gas increased sharply and continued upto 50 to 55 days of the fermentation period. After which the rate of gas generation decreased and this declination continues until the gas generation almost ceased. At the end of the 18th-week gas generation in all the reactors almost ceased.

VS removal in batch reactor

During anaerobic digestion of solid waste, biogas generation is more specifically related to the reduction of biodegradable fraction of VS in the digester. VS reduction in the test reactors was observed in the range of 34.82-50.66%. These values are comparable with the VS reductions reported in the literature for various substrates. The percentages of VS of slurry decreased with increasing digestion period. Figure 9 shows that the VS concentration is decreased with time as the part of VS consumed by bacteria for biogas generation. The percentages of the solids are correlated with the digestion time as the values of R2 are about 0.99 in all cases. The tendencies of concentrations for solids are decreasing with time. But the degree of reduction depends on the initial volatile solids concentration of the slurry. Biogas generation is a biological process and bacteria consume nutrients for cell production and energy source extracted from solids which has resulted solid reduction.

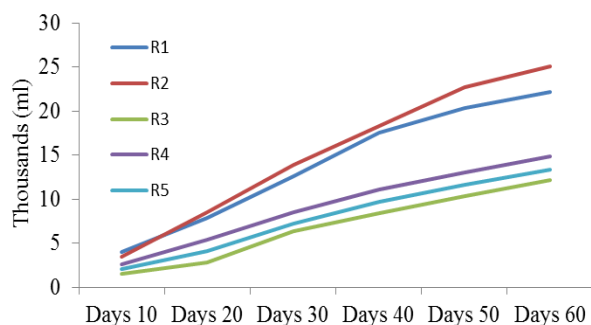


Figure 8. Cumulative gas production in different reactors

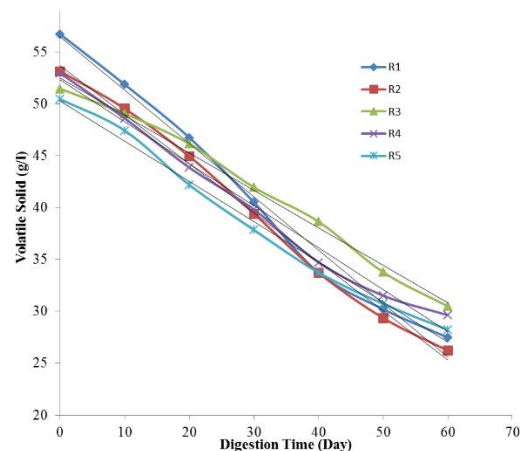


Figure 9. VS removal from different reactors

COD Removal

COD of the slurry was considerably reduced by anaerobic digestion treatment. The reduction of COD value means the reduction of pollution load from any substrate by the treatment process. The COD value curves for four different reactors are shown in Figure 10. The trend line shows, there is good correlation exist between digestion time and COD value as the R² value is above 0.98 for all the reactors. The COD removal rates for reactors: R1, R2, R3, R4 and R5 were 48.75, 50.84, 46.07, 45.94 and 47.78% respectively. In reactor R2, maximum COD removal was achieved where maximum biogas production was performed.

C/N ratio

The C/N ratio of the fleshing material is 2.51 which was very low. Therefore, cow dung and domestic sewage were used as co-substrates. The reactors were operated at C/N ratio of 17, 16, 14, 15 and 16, respectively. In fact the C/N ratios were very low in compare to standard values (20 to 30). But in this range reactors operated without any setback even at lowest C/N value R3 reactor has been given the considerable amount of gas. The C/N ratio of reactor R2 was 16 which was obtained by optimum gas production.

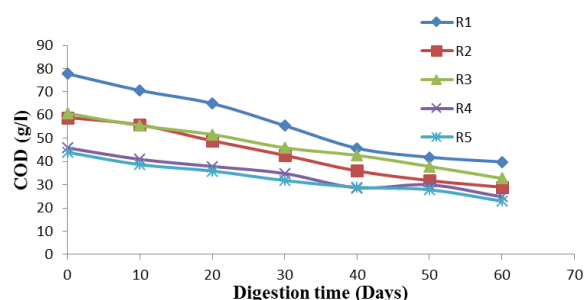


Figure 10. COD value reduction from different reactors

CONCLUSION

The present practices of disposal of tannery waste are not environmental friendly and cause great concern for Dhaka City. The solid waste fleshing contains about 81.32% VS which is amenable to biodegradation. The C/N ratio of fleshing is very low and alone is not suitable for biodegradation but mixing with other substrates with fleshing the generation of biogas is very satisfactory. The composition of reactor R2 gives the best performance for specific gas production by reducing COD and VS. In addition to this, the mixing of other substrate improves the environmental condition of the biogas reactor for desired anaerobic digestion. The methane content of biogas from the substrate was very satisfactory. The fleshing waste can be used as a complementary substrate part of small scale biogas plants. Use of fleshing will also reduce the cow dung requirement in a biogas plant which

