

Anaerobic Digestion of Tannery Solid Waste for Biogas Production: The case of Modjo Tannery, Modjo; Ethiopia

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Abstract: The present study characterized the physical property, total solids (TS), volatile solids (VS) and Carbon to Nitrogen ratio (C/N ratio) of tannery solid waste (TSW). Five different combinations with or without cow dung (CD) were assessed for their biogas production suitability in triplicate batch digesters (D-1, D-2, D-3, D-4, and D-5) with a total volume of 2.8L. The results showed that TS, VS and C/N ratio of wastes were 56.37%, 76.34% and 29.05%, respectively. The results also suggested that the highest volume of biogas (4,756 ml) with a methane content of 60.37% was produced by the digester containing 75% TSW and 25% CD and the lowest biogas (2,539 ml) with quality of 68.06% was produced by digester containing 100% CD. The average methane contents of different digesters were D-1 (100% TSW) 53.23%, D-2 (75% TSW: 25% CD) 60.37%, D-3 (50% TSW: 50% CD) 58.78%, D-4 (25% TSW: 75% CD) 57.66% and D-5 (100% CD) 67.31%. Total and volatile solid removal efficiency of all digesters was in the range of 42.27-76.34% and 47.16-79.23%. The study concluded that TSW is a good feedstock for biogas production by utilizing agro-industrial based organic solid waste for bioenergy production.

Keywords: Waste-to-energy, tannery waste management, solid waste reduction.

INTRODUCTION

Industrialization, urbanization and modernization of agricultural activities have increased the quantity of solid waste generations, thereby, causing detrimental environmental pollutions and problems. Tanning of leathers is among the oldest industries in the world [1]. During prehistoric times, tanning activities were structured to meet the resident needs of leather drums, footwear and musical instruments [2]. With the growth of population, the increasing requirement of leathers and its products led to the establishment of large commercial tanneries [3].

Even though tanning industries play an environmentally important role by giving an innovative life to the leftovers of the slaughterhouse, the conversion of this by-product is yet potentially pollution-intensive and it is broadly perceived as a natural resource consumer [1, 4]. Moreover, leather industries all over the world have been recognized closely for their negative public image because of the generation of air, liquid and solid pollutions to the environment. Though, the tanning industry is not exception to this, considerable amount of solid wastes including hazardous wastes containing chromium are generated and known for its severe impact on the environment [2, 5, 6].

The main sources of Tannery Solid Wastes (TSW) are skin trimming, fleshing, keratin, buffing and chrome

shaving wastes, which have high protein content. From 1000 kg of raw hide only 200 kg is converted to leather, where as a large amount of solid waste (800 kg) is disposed off in the surrounding environment [1, 7, 8]. If the solid wastes generated during various tanning operations are not properly utilized or managed, they are likely to cause numerous problems to the environment. Tannery industries are likely to invest massively on solid waste safe disposal mechanisms and management in future [5].

Burning and disposing of solid wastes on open landfill, releases greenhouse gases from the decomposition of organic matter. It also produces undesirable odors posing health hazards to the community [9]. The organic wastes generated by the leather industries undergo biodegradation and emit greenhouse gases, primarily methane, which is 25 times stronger than carbon dioxide and to a lesser degree of Nitrous oxide (300 times stronger than CO₂). It also causes potential odor and land contamination problems.

The problem can be managed through adoption of eco-friendly waste-to-energy recycling technologies such as anaerobic digestion (AD), which processes solid wastes before their disposal [10].

The AD process also referred to as bio-methanation is a multifaceted process, which involves many different microorganisms (conglomerates). It is a promising, mature and recognized technologic solution that has the potential to convert TSW into energy efficiently (biogas), elimination of uncontrolled methane

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emissions and odor, contributing to lessen environmental problems, safe waste management, giving time to set-up more sustainable treatment and disposal routes [10, 11]. According to Reijnders and Huijbregts [12], the potential for waste-derived bio-energy to contribute to the bargain of global warming is substantial. Moreover, AD technology can play a key role in realizing three major international environmental policy objectives: (a) Renewable Energy (b) Water Pollution Control (c) Kyoto Protocol/Global Warming.

In developing countries, the tanning industry contributes significantly towards exports, employment opportunity and plays an important role in the economy. In view of this, the present research was aimed to study the efficiency of AD of TSW for biogas production and waste management.

MATERIALS AND METHODS

Feedstock (Substrates) and Its Composition

The feedstock (substrates) used for the biogas production at bench scale were TSW and cow-dung (CD) mixed at different ratios. TSW (skin and trimming) samples were collected from Modjo Tannery Share Company, Modjo Town, which is 70 km from the capital city Addis Ababa. About 10 kg of CD was obtained from a private dairy farm at the vicinity of Sululta town: North Shewa, Oromia, Ethiopia, which is 25 km from Addis Ababa. Approximately, 5000 ml of inoculums was taken from an operating biogas plant at the College of Natural Sciences; Addis Ababa University. All the feedstock's were kept at 4°C in the refrigerator at the Laboratory of the Center for Environmental

Science, until used. To increase the surface area of the substrate (TSW) it was pre-treated (cut into pieces) according to Badger *et al.* [13].

Biogas production potential and quality of the gas produced were evaluated at five different treatments combinations of TSW and CD using a bench scale digester. The following ratios were the five treatments used in the study; D-1 (100% TSW), D-2 (75% TSW: 25% CD), D-3 (50% TSW: 50% CD), D-4 (25% TSW: 75% CD) and D-5 (100% CD) on the basis of (w/w)%. The amount of total solid (TS) of each treatment was kept constant at 100 g and the amount of water added was as recommended by Ituen *et al.* [14], so that the TS in the digester is 8%. Each treatment was run in triplicate and 100 ml of inoculum were added to kick-up the reaction.

Feedstock Physico-Chemical Property Determination Methods

Total solids (TS), volatile solid (VS) were estimated using APHA, 1988 [15] and Carbon to Nitrogen ratio (C/N) was determined as of [16].

Bench Scale Anaerobic Digester

Bench scale anaerobic digesters were prepared in the Research Laboratory of the Center for Environmental Science; Addis Ababa University. Amber bottles of 2.8 L holding capacity was used as bench scale digesters. To create the anaerobic condition, the bottles were covered with a rubber stopper with two outlets and sealed with a gas kit, so that it is confidently air tight. Two gas pipes of 8 mm

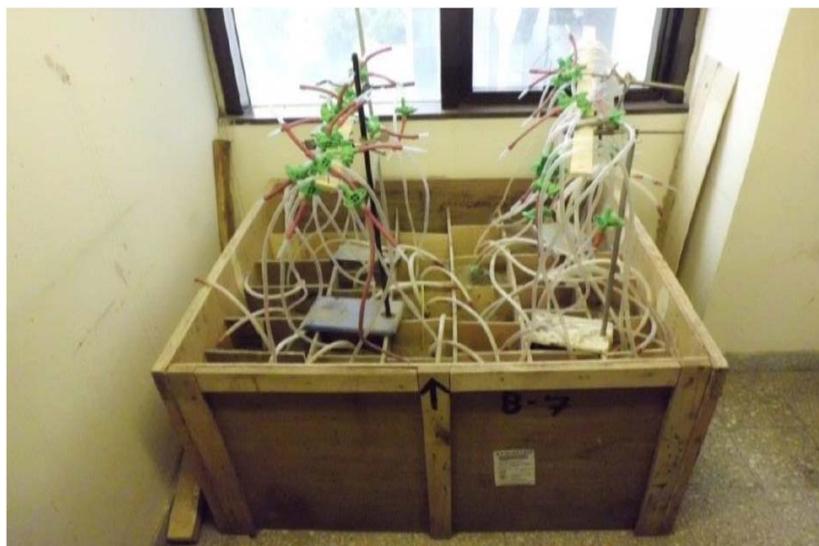


Figure 1: Bench Scale Sand-Jacketed Anaerobic Digester Setup Placed in the Partitioned Box.

internal diameter, with lengths of 0.5 m and 1 m were immersed in the digesters. The 0.5 m long hose was stretched up to the bottom of solution to measure the pH of the slurry, while the second one above the slurry was used to off-take the gas from the digesters for biogas measurement during the AD processes. The 0.5 m hose was sealed by pipette tip while the 1m long hose was controlled by a valve. The room temperature fluctuation was regulated by sand-jacketing the digester, which was placed in the partitioned boxes (Figure 1).

Quantity and Quality of Biogas

The biogas produced was determined by water displacement method, while the quality of the biogas was done by biogas analyzer (Geotechnical instruments (UK) Ltd, S/R: BM 14068). The amount (quantity) of biogas from the digesters was taken to a volumetrically calibrated collector vessel (measuring cylinder) filled with water, which was kept under pressure. When the biogas entered the cylinder filled with water from the top, the pressure of the biogas forced the water into the empty beaker. The volume of the water displaced indicated the total biogas produced. The total biogas produced for each treatment was calculated by deducting the share of inoculums to know the contribution of each digester. The total amount of biogas produced from each digester presented in this paper is the net biogas produced throughout the digestion periods.

The quality of biogas (percentage of methane) was measured weekly using a biogas analyzer, until the gas production ceased. The hose that channeled the gas was directly connected to the calibrated biogas analyzer and the percentage of methane was displayed on the analyzer. Combustibility of the biogas was also seen by connecting the gas line to a Bunsen burner.

RESULTS AND DISCUSSION

Characterization of Feedstock's for Biogas Production Parameters

The averaged values of TS, VS and C/N ratio of the feedstock are presented in Table 1. For CD, the TS

obtained in this study are in the range of (15-20%), which is similar with the results reported in Fulford [17]. The VS as percent of TS for CD is 87.67%, the result come close to the earlier findings of 86.77% reported by Ali *et al.* [18] and 86.73% by Li *et al.* [19]. However, the result of this research is higher than the value reported by [17], which was 77%. The VS values for each feedstock in the present study varies from 76.34 - 87.67%, which is within the range of 60 - 87% as reported by Zolar *et al.* [20], (Table 1).

The variables given in Table 1 are among the main factors that affected the AD processes, the amount and quality of biogas produced. Therefore, these parameters are also an indication of the suitability of the feedstock for biogas production [17-21].

The C/N ratios of different digesters were 29.05, 21.48, 19.49, 18.6 and 18.14 for digesters D-1, D-2, D-3, D-4 and D-5. The C/N ratio of the digesters decreases as the ratio of TSW decreases from 100% to zero. The C/N ratio of digesters D-1 (29.05) and D-2 (21.48) are in the range of C/N ratio of 20 to 30 as stated by Braun [22], Dahlman and Frost [23], for the digesters to yield optimum biogas. However, the C/N ratio of D-3 (19.49), D-4 (18.6) and D-5 (18.14) are lesser than previous studies. In another study [21], it was mentioned that C/N ratio of the feedstock is in the range of 10–30, which is similar to the present study results (Table 1).

The Working Conditions of AD Process

Temperature and pH largely affect biogas production and its quality. These two parameters (Temperature and pH) were given due considerations for better biogas production in this study. The results for these two parameters are given below.

Temperature

The average daily room temperatures during the course of the digestion period was low and it was in the range of 14.5–23.2^oC (Figure 2). The ambient temperature range during this study was 15-25^oC, which can be regarded as temperate climate. The

Table 1: Characteristics of the Averaged Feedstock in Terms of Biogas Production Parameters

Parameters Feedstock	Moisture Content (%)	TS (%)	VS% on basis of TS	Ash % on basis of TS	OC (%)	TN (%)	C/N ratio
TSW	43.63	56.37	76.34	23.66	42.41	1.46	29.05
CD	84.22	15.78	87.67	12.33	49.53	2.74	18.08

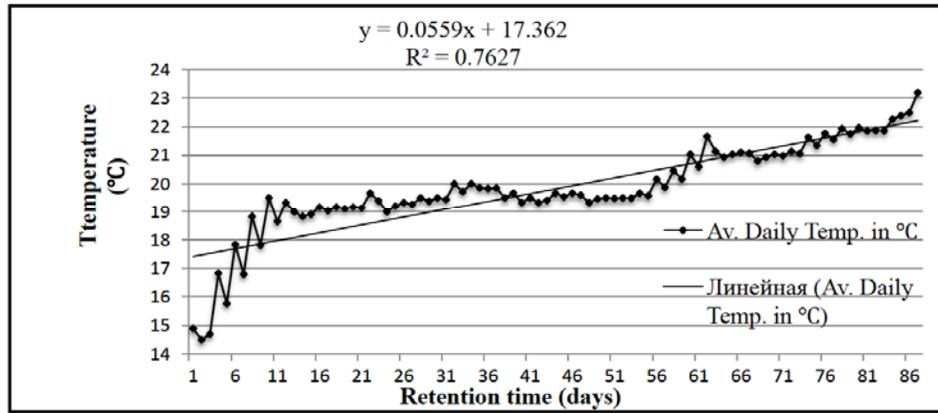


Figure 2: Average daily room temperature of the laboratory.

average room temperature was fluctuating initially for about two weeks; afterward it become more or less constant for two months and then it started to increase up to the end of the experiment (Figure 2). It is pertinent to note here that the experiment was started at the end of the winter season, where colder temperatures were experienced during morning hours. Therefore, the temperature trend showed low average room temperatures during the first two weeks of the study.

Also from Figure 2, it is can be seen that the room temperature fluctuation was about 8.7°C, which can be regarded as an extreme fluctuation that may affect the metabolic activities of microorganisms. According to Ozmen and Aslanzadeh [24] the specified limits for fluctuation should not exceed $\pm 2^\circ\text{C}$ for the psychrophiles (below 20°C). However, NRCS [25] recommended that the fluctuation of ambient temperature can be minimized by thick covering/jacketing of the digester by sand of about 10 cm radius, which will bring digesters temperature

fluctuation to less than 1°C. Subsequently, in the present study, to minimize the temperature fluctuations, the digesters were sand-jacketed in a wooden box prepared by partitioning the chambers with radius of about 20 cm.

The trend analysis for the temperatures indicated a significant increase from the 1st day to the 87th days of the retention time (Figure 2). The regression (R^2) showed a significant value of 0.76, indicating the reliability of the data. Thus, the study suggested that even at lower temperature (14.5-23.2°C), there is possibility of producing biogas by sand-jacketing the digesters to control temperature fluctuation, however, the retention time period increased to 87 days. Earlier studies by Jigar *et al.* [26] mentioned that the lower the temperature, the longer the retention time (62 days).

pH

The average pH variations of each of the digester during the reaction period (retention time), which were

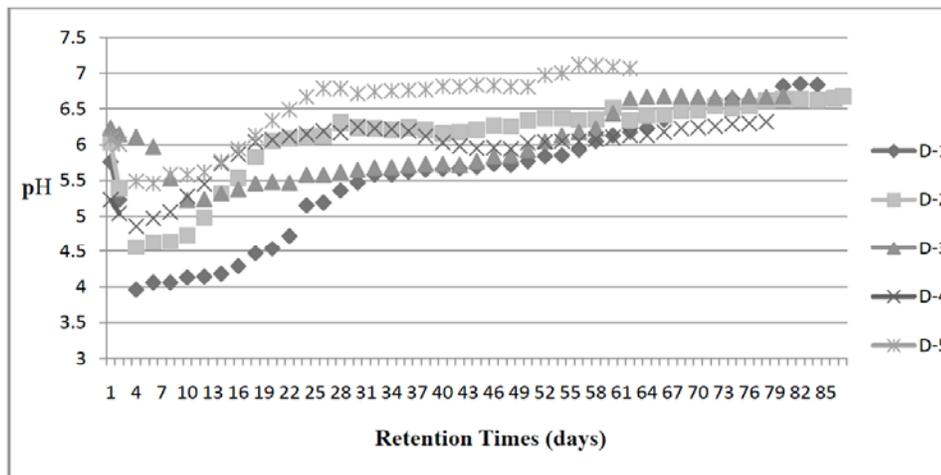


Figure 3: Average pH values of the digesters throughout the retention time.

taken at two days time interval is given in Figure 3. The figure indicates that the pH value of each digester dropped in a few days of the reaction time. The drops in the pH is due to organic acid formation which is an indication for the system start up and increases as the methanogenic bacteria consumes the acids produced in the acidogenesis and acetogenesis steps for the production of biogas [27].

The decrease in pH is also the function of the concentration of volatile fatty acids (VFA) produced by the activity of hydrolytic acidogenic bacteria capable of degrading the feedstock in the first few days of incubation, bicarbonate alkalinity of the system, and the amount of carbon dioxide produced [28]. Nina *et al.* [29] verified that, the presence of fat content can raise the formation of VFA, leading to a fall in pH. The present study showed that the overall pH of digesters containing TSW was lower than the digesters containing CD alone until the gas production ceased. The result, thus indicates that it is feasible to produce biogas from tannery waste co-digested with CD in the pH range of 3.96 to 7.11 (Figure 3).

Amount of Daily Biogas Produced

The output of the average daily biogas production of each digester for about thirteen week is shown in Figure 4. The figure showed that the rate of averaged daily biogas production (volume) in almost all digesters increased persistently up to the fifth week, with the exceptions of D-2 and D-3 the increments continued up-to the seventh week. The maximum and minimum reaction time periods were recorded as 87 days for D-2 (75% TSW: 25% CD) and 62 days for D-5 (100% CD). The longer reaction time period is due to the feedstock's lower bioavailability, though its theoretical biogas yield is high. On the other hand, the slow increased of the daily averaged room temperature after

two weeks during the reaction time period may be the reason for the increase of the daily averaged biogas production. Christy E. [30] mentioned that an increased in temperature has a positive effect on biogas yields.

Maximum amount of biogas were produced during the 5th and 6th weeks of digestion periods; afterwards the biogas production gradually decreased (Figure 4). The highest values of daily biogas yield in each digester were during the 36th to 46th days of digestion period. The maximum values were 195, 192, 211, 184, and 179 ml from D-1, D-2, D-3, D-4 and D-5, respectively. Moreover, the maximum biogas was produced between the first and nine weeks of the reaction period in all the digesters which was in the range of 100–295 ml except D-5. The daily averaged biogas production in all digesters showed similar trends of gradual increments to maximum and then decreased slowly till it ceased to produce further biogas (Figure 4).

Total Biogas Production

Biogas production was measured for about 13 weeks of digestion period, until gas production ceased. The total biogas produced during the reaction period for all digesters is presented in Figure 5. The study showed that D-2 with 87 days of reaction period produced the highest total biogas (4756 ml) and D-5 with 62 days of reaction period produced the least (2539 ml) (Figures 4 and 5). Digesters D-1, D-3 and D-4 produced 3972, 4479 and 4183 ml of biogas, respectively. It is well known that the composition of biogas as well as biogas yields depend on the substrates owing to differences in material characterization in each feed [30]. In the present case, the highest biogas produced by D-2 may be due to its C/N ratio of 24.18 (Table 1), which is in the range of C/N ratio value for digesters to produce the optimum biogas [22].

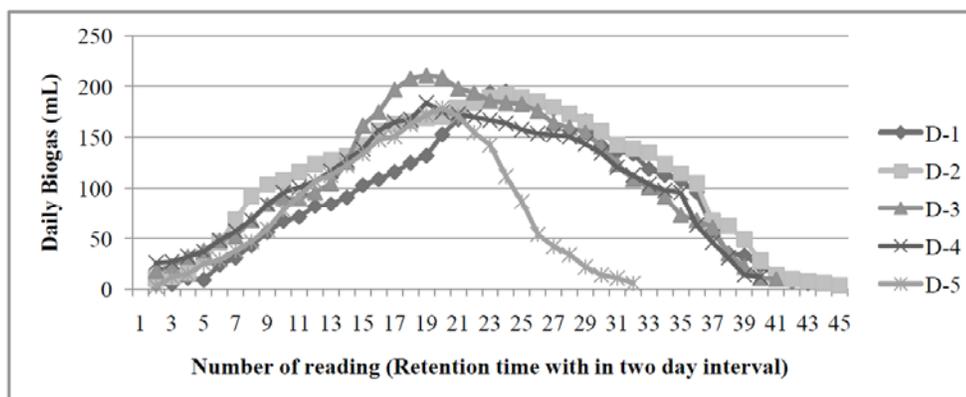


Figure 4: The average daily biogas production potential of each treatment.

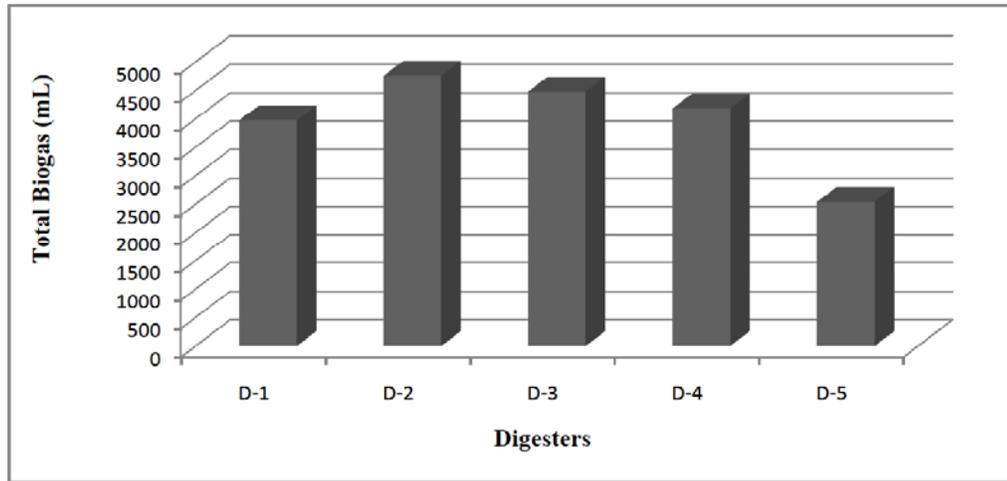


Figure 5: Comparison of total biogas production of different digesters.

The daily averaged biogas production rate can be obtained by dividing the total biogas by the respective retention time. Therefore, the daily biogas productions of D-1, D-2, D-3, D-4 and D-5 are 48.44, 54.67, 55.99, 53.63 and 40.95 ml/day, respectively.

Quality of Biogas Produced

Figure 6 below shows the weekly biogas quality produced by each digester. As it is shown in Figure 6, the quality of biogas produced by each digester in the first week of digestion period was below 50%. This indicates that, it cannot be combustible during this reaction period unless the biogas quality is enhanced by using different scrubbers to absorb the other component of the biogas like CO₂ and other trace gases like H₂S. Digesters D-1 and D-2 continued to produce biogas with quality of less than 50% until the end of 2nd and 3rd week of reaction period, respectively.

Except for D-1 and D-2 the quality of the biogas remained in the range of 50 to 80% in most of the digesters from the 1st week up to the end of the digestion period (13th week). In view of that, the result of the quality of biogas of this research revealed that after the first week it is combustible except for D-1 and D-2 where the combustibility started from the 3rd and 4th weeks. In addition, depending on the system design and the type of waste feedstock, 55 to 75% of biogas is pure methane [32-33] which is in agreement with the results of this study (Figure 6).

The cumulative biogas quality produced by other digesters D-1, D-2, D-3, D-4 and D-5, were 53.23%, 60.37%, 58.78%, 57.78% and 67.31%, respectively. The highest and lowest cumulative biogas quality was produced by D-5 (100% CD) 67.31% and D-1 (100% TSW) 53.23%, respectively. Moreover, the overall biogas quality produced by all digesters was in the

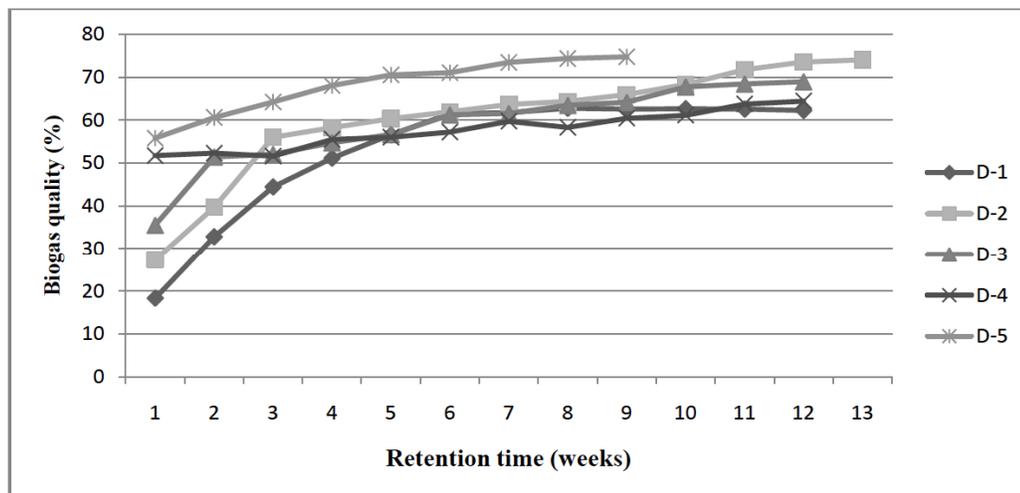


Figure 6: The Weekly Percentage of Biogas Quality Produced by Each Digester.

range of 55-75%. It is in the range of biogas quality reported by Curcio *et al.* [34] greater than 50%, 50-70% reported by Yadav and Hesse [35] and 40-80% suggested by [31]. Therefore, this result has revealed the possibility of producing high quantity and quality biogas from TSW without addition of other co-digesters except a starter (inoculant).

Characteristics of the Digestate after AD

Solids Reduction after AD

The TS and VS of each digester after the digestion period are indicated in the Table 2. Anaerobic treatment of wastewater converts the organic pollutants into a small amount of sludge and large amount of biogas (methane and carbon dioxide). The relative higher removal efficiency of VS (%) than TS (%) in all digesters was a very good indication of high uptake rate of the organic fraction of TS and the effectiveness of the anaerobic reactor in digesting tannery waste under AD during proper operating conditions. Fifty to seventy five percent of the original TS were converted to gaseous form, leaving 25-50% as anaerobically digested solid residues by AD (Table 2), [35].

From the percentage reduction of TS and VS, it can be put forward that AD can reduce the amount and volume of tannery waste which is disposed in dumpsites. It can also reduce the cost of transport as well as the task of the solid waste management sector.

Comparison of the volatile and total solid before and after digestion gives an indication of the utilization of the organic content in the reactor. Similarly, VS/TS ratio of TSW before and after digestion was 1.49% and 1.03%, respectively. Generally, the ratio of VS/TS before digestion was always relatively higher than the ratio after digestion, which is an indication of the utilization of the organic fraction during the anaerobic digestion; which is true for all the digesters in this study.

Capturing and combusting methane with anaerobic digesters offers two benefits from a greenhouse gas emissions point of view. First, since methane has a significantly higher global warming potential than CO₂, combusting methane, rather than releasing it directly into the atmosphere, decreases the direct greenhouse gas (GHGs) emissions. Second, when the combustion process is used to generate heat or electricity, it displaces fuel consumption which impact of would have occurred in the absence of the digester, creating an indirect emissions reduction. Hence, through

converting waste to energy, AD has a potential of mitigating GHG emission that contributes to climate change [36].

CONCLUSIONS

The findings of this study show that tannery solid waste is a potential feedstock for anaerobic digestion. The ranges of mean daily room temperature and the pH during the course of the anaerobic digestion period were 14.5 to 23.21⁰C and 3.96 to 7.21. The results of the temperature and pH indicate the feasibility of producing biogas from tannery waste by sand-jacketing the digesters and co-digesting the solid wastes with cow-dung. The tannery solid waste (75%) blended with cow-dung (25%) produced higher amount of biogas (4756 ml) with 60.37% methane quality. The relative average percentage removal of total solid (42.27 to 76.34%) and volatile solid (47.16 to 79.23%) were found for all digesters, indicating significant reduction in the volume of tannery wastes produced in the industry. The present research will help provides benefit of waste management, renewable energy generations (biogas) and reduction of greenhouse gas (CH₄) by tannery industries in temperate and high altitude regions of the world.

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