Biogas potential from spent tea waste: A laboratory scale investigation of co-digestion with cow manure

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Abstract

Spent tea waste (STW) is an organic waste that is disposed in open land after preparation of tea. Generally, it is disposed in an open land which increases anthropogenic gases. Converting it into useful energy or value added product may reduce disposal problem and anthropogenic activity. In this study, STW was co-digested with cow manure (CM) for obtaining biogas by anaerobic digestion. For this purpose, STW was mixed with CM at different proportions, namely 50:50, 40:60, 30:70, 20:80, and 0:100 percentages on a mass basis, were used in five different anaerobic digesters. The samples were kept in different anaerobic digesters for the study. The effect of important input parameters like pH, Carbon to Nitrogen (C/N), and digestion time on the biogas production were studied. Further, the collected biogas from the digesters were characterised to ensure the suitability for use as a renewable fuel. Furthermore, the digested slurry was also analysed for its use in agriculture sector. The results are presented in this paper.

Keywords: Spent tea waste, Cow manure, anaerobic digestion, biogas

Nomenclature

STW	Spent Tea Waste
CM	Cow Manure
AD1	Anaerobic Digester1
C/N	Carbon to Nitrogen
CH_4	Methane
NH_3	Ammonia
CO_2	Carbon dioxide
H_2S	Hydrogen Sulphide
MSW	Municipal Solid Waste
NIT	National Institute of Technology
FTIR	Fourier Transform Infrared Spectrography
O	Oxygen
H	Hydrogen
Br	Bromine
I	Iodine
Cl	Chlorine
TS	Total Solid
VS	Volatile Solid

ml	Millilitre
kg	Kilogram
kW	kilowatt
Vol.	Volumetric
MJ	Mega Joule
N/K	Nitrogen to Potassium
N/P	Nitrogen to Phosphorous
Fe	Ferrous (iron)
Zn	Zinc
Ni	Nickel
Co	Cobalt
GHG	Greenhouse gases

1 Introduction

Global warming and ozone depletion are the two major threats to the world. Pollutants resulted from combustion of fossil fuels and the anthropogenic gases released from dumping of organic wastes into open land are believed to be the main reasons for global warming. Some of the measures are being taken by many countries to control global warming are (i) adopting emission reduction techniques for combustion devices (ii) using renewable alternative fuels (iii) effective waste management [1]. Organic wastes are present in the form of biomass waste, animal waste, municipal waste and industrial waste. Biomass waste is largely available in the form of bushes, straws, residues, leaves, seeds etc. Industrial wastes include fodder and brewery industries, food and fish processing, starch, milk, sugar, pulp and paper, pharmaceuticals, biochemical and cosmetics, as well as slaughterhouses. The examples of municipal wastes are garden waste, food waste and other organic wastes [2].

Spent tea leaves, spent tea waste, and spent coffee powder, are the type of organic wastes significantly available in houses, restaurants, hotels, refreshment stalls throughout the world. Some documents in the form of research articles are available on obtaining energy or fuel from spent tea leaves [3] [4], spent coffee powder [5] [6], and still there is a need to explore more possibilities of converting such residues into useful energy.

There are two main methods adopted for converting organic wastes into energy or fuels are; (i) thermochemical conversion and (ii) biochemical conversion. Example of thermochemical conversion includes direct combustion, pyrolysis and gasification. The examples of the biochemical conversion are anaerobic digestion and fermentation. Biochemical conversion is the most suitable technique for a maximum recovery of energy from organic wastes [7]. It can be used when an organic waste is almost free from metals. Among the biochemical conversion methods, anaerobic digestion is a well-recognised and proven technology by which biodegradable organic matters are decomposed with the help of bacteria in the absence of air, creating biogas as a by-product. In an anaerobic digestion process, process stability is very important. Sometimes, instability occurs between the micro-organisms is due to inhibition. Inhibitory substances like sulphide, ammonia, heavy metals like Fe, Zn, Ni, Co, chromium, mercury, lead and manganese, organic compounds include chlorinated hydrocarbons, benzene ring compounds, cyanides, phenols and alkyl phenols, lignin related compounds, organic acids (long fatty acids and amino acids), citrus oils (limonene) etc., will adversely affect the anaerobic digestion process [8] [9]. Owing to high energy recovery and limited environmental impact, anaerobic digestion is widely used for the conversion of different organic wastes into energy or fuel.

Biogas is a renewable gaseous fuel obtained from the anaerobic digestion of variety of feed stocks that originate from agriculture, municipal and industry [10]. Biogas obtained from a single feed stock mainly depends upon the feed stock characteristics. Co-digestion involves the mixing of two or more different feed stocks in a suitable proportions to obtain a complementary characteristics of the feed stocks. Many research papers have been published on the performance of anaerobic digesters using different organic wastes. Co-digestion offers a few advantages such as dilution of inhibitory wastes, supply of sufficient nutrients, and initiation of positive synergism in digester medium and enhancement of biogas production [11]. Only a few papers dealt directly with the co-digestion of animal manure which are discussed in the next paragraph.

An investigation was carried out by Zhai et al. [12] to study out the effect of pH (6.0-8.0) anaerobic co-digestion of kitchen waste with cow manure that was carried out in a laboratory scale digester. The results revealed that, the pH values in the range of 7.7-7.9, increased the biogas production yield. Finally, the experimental results were compared with those of the results obtained from a modified Gompertz equation. A study was carried out by Riggio et al. [13], to assess the feasibility of biogas production by mixing cow slurry with olive pomace and apple pulp. It was concluded that, a mixture containing 85% cow slurry, 15% olive pomace, 5% apple pulp gave a better yield. It was also concluded that, a stable biogas production was obtained at a digestion time of 40 days. Food wastes are largely available year round and have the potential of biofuel production. Many researchers studied on the digestion of food waste for obtaining energy or fuel. For instance, co-digestion of cow manure and food waste balances the nutrients in an anaerobic digester, and thus providing a more stable environment for the growth of anaerobic bacteria [14]. In another study, thermophilic anaerobic digestion of cattle manure and pasteurised food waste was assessed in batch and high volume lab scale digesters [15]. During this study, it was found that, the specific methane production increased by about 86%, and a reduction in volatile solid (VS) by about 35.2% when compared to the monodigestion of cattle manure. To enhance the performance of the anaerobic digester, various pre-treatment techniques can be employed. Song et al. [16], conducted the experiments by pre-treating wheat straw with H_2O_2 at different concentrations viz., 1%, 2%, 3%, and 4%. The pretreated feed stock was co-digested with the dairy cattle manure at different ratios. It was concluded that, wheat straw treated with 3% H_2O_2 was the optimal concentration. Also, the methane yield was found to be higher with the co-digestion of treated wheat straw than untreated wheat straw or dairy cattle manure alone. Most recently, a few articles have been published on the anaerobic co-digestion of livestock manure with the organic wastes are cow manure with barley [17], cow manure with sugar beet by-product [18], dairy manure with tomato residues and corn stover [19], cow manure with kitchen waste and water hyacinth [20], goose manure with alkali solubilised wheat straw [21], chicken manure and pig manure with corn stover and apple pulp [22], and sheep dung with waste paper [23]. The results of all these studies significantly improved the biogas production.

The main aim of this study was to make an attempt to use the spent tea waste (STW) as a co-substrate in combination with cow manure for production of biogas. For this purpose, STW was mixed with CM at different proportions in five different anaerobic digesters like AD1, AD2, AD3, AD4, and AD5. Further, the study was aimed to evaluate the various affecting parameters on the biogas production. Finally, the samples of biogas obtained from the digesters were characterised to ensure the quality for using it as an alternative gaseous fuel. Further, the digested slurry was also analysed to utilize as a fertilizer for growth of crops.

1.1 Potential of spent tea waste

Tea is one of the most popular and lowest cost beverages in the world, and is consumed by a large number of people. Majority of the tea producing countries are located in the continent of Asia where China, India, and Sri Lanka are the major producers. Today, the four major tea producing countries in the world are China, India, Sri Lanka and Kenya. On an average, these countries together produce about 75% of world's production. India is the second largest producer of tea in the world, producing an average of about 900,000 tonnes every year. It is estimated that about 70 percent of tea is consumed in India only. Owing to its increasing demand, tea is considered to be one of the major components of world beverage market. Global tea production is increased by about 110% from the year 1995 to 2015 due to its increased consumption [24]. This gives a rise to a huge amount of spent tea wastes which leads to serious waste management issues. As reported in [24] by Chang, India is one among the top 5 per capita tea consumers. A number of renowned teas, such as Assam and Darjeeling, also grows exclusively in India. A snapshot of spent tea waste used in this study is shown in Fig.1. The current status of Indian tea in the global position is given in Table 1.

Table 1 Present status of Indian tea in global position [25]

	World	India	Rank	% Share
Area under tea (Million hectares)	3.94	0.58	2nd	15
Yield (kg/hectare)	1143	1668	NA	NA
Production (Million kg)	4162	966	2nd	23
Consumption (Million kg)	3980	837	2nd	21
Export (Million kg)	1738	193	4th	11

*NA-Not available

Spent tea waste (STW) is disposed in the form of slurry in open land after preparation of tea, and is one of the potential organic wastes that is abundantly available in restaurants, hotels, hostels, and almost all the houses release this waste, especially in India. A continuous disposal of STW in open land increases anthropogenic gases, pollution of soil, water, and unpleasant surroundings etc [26]. Therefore, it is necessary to find a solution to reuse or recycle of STW. Biogas production is a very efficient way to address the foresaid issues [27] both through production of renewable energy and through avoidance of uncontrolled release of greenhouse gases (GHG) emissions into the atmosphere during STW management.

Fig.1 Spent tea waste used in this study

2 Materials and methods

2.1 Feed stock

The fresh cow manure (CM) was collected from a local farm house near NIT Rourkela campus, Odisha, India. The visible straws present in the CM were removed manually. The collected CM was mixed with water in the ratio 1:1, stirred for 10min at 2000rpm, and filtered with a nylon grid of size 0.25mm. The filtrated one was used as a feed for the anaerobic digestion process. On the other hand, STW was collected from various hostels, and canteens in the institute. The collected STW was dried for 48 h at 80^{o} C and stored at room temperature in a dry place for further experiments.

2.2 Experimental setup and design

In this research work, experiments were conducted in laboratory scale anaerobic digesters namely AD1, AD2, AD3, AD4, and AD5 containing 50:50, 60:40, 70:30, 80:20, and 100:0 on a mass basis of CM: STW respectively. The prepared samples of CM:STW mixture were diluted with water at a ratio of 1:1 and 1:3 respectively. The characteristics of the feed stocks at different proportions of CM and STW are given in Table 2. The prepared samples were in a kept in a 2L glass reactors and air tight sealing was done using M-seal (epoxy compound). The anaerobic digesters used in this study are shown in Fig.2. In general, CM is the most commonly used feed stock for the production of biogas; hence, in this study, CM was also taken as a feed stock in a separate digester. The results obtained from the four different proportions of CM and STW were compared with 100 % CM. The experiments were conducted at a mesophilic temperature range ($310 \pm 2.0\,K$). All the reactors were flushed with nitrogen for 5 min before sealing of the digesters. Since, there is no mechanical stirrer available in the laboratory for stirring the mixture. Therefore, for obtaining a better reaction mixture, manual shaking was done. Each digester was shaken manually for 1 min twice a day prior to the measurement of biogas volume [12] [28].

Table 2 Properties of feed stocks at different proportions of CM and STW

Parameters	Digester name (mass fraction %)				
	AD1	AD2	AD3	AD4	AD5
	50:50	60:40	70:30	80:20	100:0
TS (wt%)	58.62	48.72	42.67	36.55	19.26
VS (wt%)	52.48	45.61	39.54	32.42	15.23
VS/TS ratio	0.89	0.93	0.92	0.88	0.79
Weight of CM added (g)	200	240	280	320	400
Weight of STW added (g)	200	160	120	80	--
Volume of water (ml)	800	720	640	560	400
Total weight of substrate (g)	1200	1120	1040	960	800

AD1-AD5 anaerobic digesters; 6-10 biogas to analyser; 11-15 scale for water level indicator

Fig.2 Anaerobic digesters used in this study

2.3 Biogas measurement and its composition analysis

Biogas production was measured by the water displacement method in a U-tube manometer (outer diameter 1.8cm and 0.25 thickness) in an interval of 24 hours during 25 days of digestion time. To measure the composition of gas produced, a sample of gas was collected daily from the headspace of each digester using gas tight syringe (25 µL Perkin Elmer), and then injected into GC equipped with a stainless steel column of TDX-01 (packed with carbon molecular sieve, 2 m × 3 mm) and a thermal conductivity detector (TCD). The temperatures of the column oven, injector, and detector were 100 °C, 150 °C, and 175 °C, respectively. Argon was used as a carrier gas at a flow rate of 20 mL/min. Biogas majorly consists of CH_4, CO_2, and a trace amounts of H_2S, and NH_3. Biogas composition was measured daily, in terms of percentage volume (%vol), as per the test method (ASTM D 7833). Also, the properties of biogas includes density, energy content, lower heating value, boiling point were characterised according to the ASTM standards D 3588, 4868, 1945, 1835 respectively.

2.4 Analytical methods and calculations

Firstly, feedstock characterization was carried out to ensure the suitability of the feed stock for anaerobic digestion, which included the proximate and ultimate analyses. The proximate analysis of all the samples was calculated in the Chemical Engineering Department of NIT Rourkela, as recommended by APHA [29] and are given in Table 3. The ultimate analysis of the samples was done by a C-H-N-S elemental analyser in the Chemistry Department of NIT Rourkela, and are given in Table 4. The C/N ratio was determined by dividing the total carbon content to the total nitrogen content. The pH value of the feed stock was measured with a pH metre (Systronics µ pH system 362). Various characteristic functional groups present in the substrate were identified by a Perkin Elmer RX Fourier Transform Infrared spectrograph (FTIR) in the Mining Engineering Department of NIT Rourkela. The FTIR results were collected in the range of 40 – 4000 cm^{-1} with the resolution of 8 cm^{-1} which is discussed in a separate section. Further, the concentrations of Phosphorous (P), and Potassium (K) present in the digester were determined using inductively coupled plasma mass spectrometry, from a standard laboratory (Advanced research and testing laboratory, Kolkata). All the experiments were conducted thrice to find out its average. The methane yield expressed in terms of ml/kg TS was calculated by multiplying the total biogas production with the methane content obtained from GC in %vol, divided by 100.

Table 3 Proximate analysis of CM and STW

Substrate	Weight % dry basis			
	Moisture content	Volatile matter	Ash content	Fixed carbon
Cow manure	71.2	12.3	4.37	12.13
Spent tea waste	9.36	42.33	8.8	39.51

Table 4 Ultimate analysis of CM and STW

Substrate	Weight % dry basis						
	%C	%H	%N	%S	%O	%P	%K
Cow manure	36.23	4.76	1.67	0.03	57.2	0.05	0.06
Spent tea waste	63.3	6.45	0.97	0.48	26.6	0.8	1.40

2.5 FTIR spectra of the feed stocks

Basically, FTIR determines the different types of functional groups and bonds that are present in a molecule, using infrared electromagnetic radiation. The functional groups present in CM and STW are depicted in Fig. 3. It can be observed from the figure that, such peaks (broad, and sharp) observed at various intensities reveal the presence of different functional groups. The group compounds present at different intensities in the feed stocks are listed in Table 5.

The broad peak observed in the range of 3800-3200 cm^{-1} mainly represents the presence of phenols, alcohols, and hydroxyl acid, and is caused by O-H, N-H stretching. The C-H bond stretching vibration from 2960-2850 cm^{-1} represents the sharp edge with medium intensity, indicates the presence of alkanes.

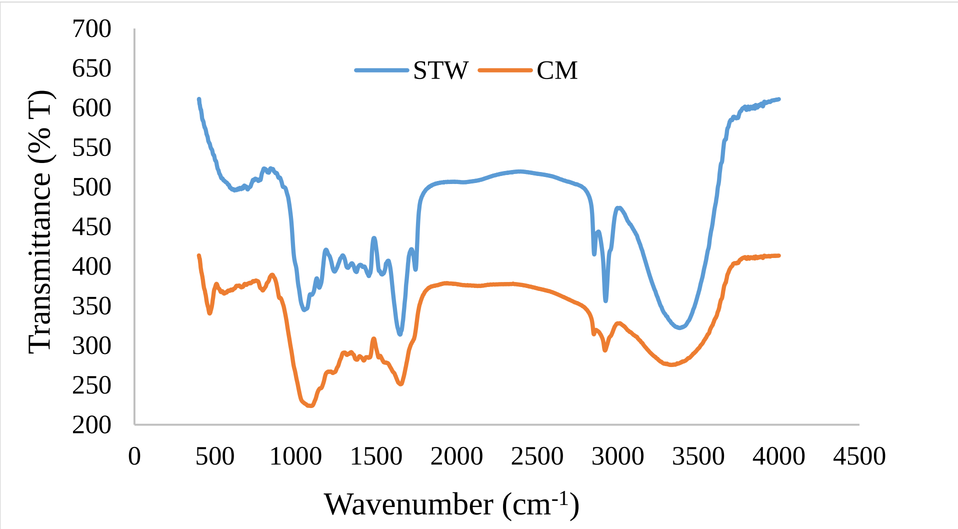

Fig.3 FTIR spectra of STW and CM

A sharp peak at 1649.11 cm^{-1} arises from C=O stretching, which indicates the presence of ketones. A peak at 1455 cm^{-1} represents the presence of alkyl methylene due to C-O, C-H, and N-O stretching. Furthermore, the region from 0-1500 cm^{-1} is known as finger print region, which indicates a cluster of stretches in one region. It refers to the mono cyclic substituted aromatics with C-Cl, C-Br, C-I, and O-H bending. From this study, it was concluded that, the feed stocks were suitable for anaerobic treatment, as they contain ingredients for the growth of microorganisms.

Table 5 Feed stocks' FTIR spectra

Wavelength range, cm^{-1}	Peak		Functional group	Type of vibration
	STW (cm^{-1}, %T)	CM (cm^{-1}, %T)		
3500-3300	3384.96 , 322.08	3332.62, 275.49	Phenols, Alcohols, Hydroxyl acid	-OH, N-H stretching
2960-2850	2924.82 , 356.03 2854.07 , 414.92	2920.82 , 293.68	Alkane (fully saturated)	C-C, C-N, C-H stretching
1740-1550	1744.61 , 395.65 1649.11 , 313.77 1538.26 , 389.68	1654.51 , 251.14	Ketones	C=C, C=N, C=O stretching
1470-1250	1455.00 , 387.68 1377.90 , 392.70 1242.34 , 393.29	1423.48 , 281.00	Alkyl	C-O, C-H, N-O stretching
1150-500	1147.31 , 372.94 1053.62 , 344.70 620.80 , 495.67	1094.88 , 223.72 796.49 , 369.45 555.72 , 365.52 466.76 , 340.41	Mono cyclic substituted aromatics	C-Cl, C-Br, C-I, O-H bending

3 Results and discussion

3.1 Effect of pH

One of the most important parameters that affect the biogas production is the pH value of the slurry. pH value changes at different stages of anaerobic digestion. Kigozi et al. [30] reported that, most of the anaerobic bacteria performs a good yield, if the pH value lies between 7-8.5. During the initial stages of anaerobic digestion, the pH value of the substrate rapidly drops because of digestible matter get hydrolysed and converted into fatty acids. Due to the formation of huge amount of fatty acids, sometimes, pH value may fall below 5 in the digester. In general, an increase in pH accompanies when the consumption of fatty acids by methanogens and thus produces alkalinity [31]. It was reported by Mshandete et al. [32] that, for a normal functioning of an anaerobic digester, the pH value is in the range of 6.4-7.6. Beyond this stated range, the biogas process will become more sensitive towards the concentration of ammonia with increase in pH. Because of which, the growth rate of microbes decreases. Fig.4 portrays the variation of pH with the digestion time by considering the average value of pH in every five consecutive days.

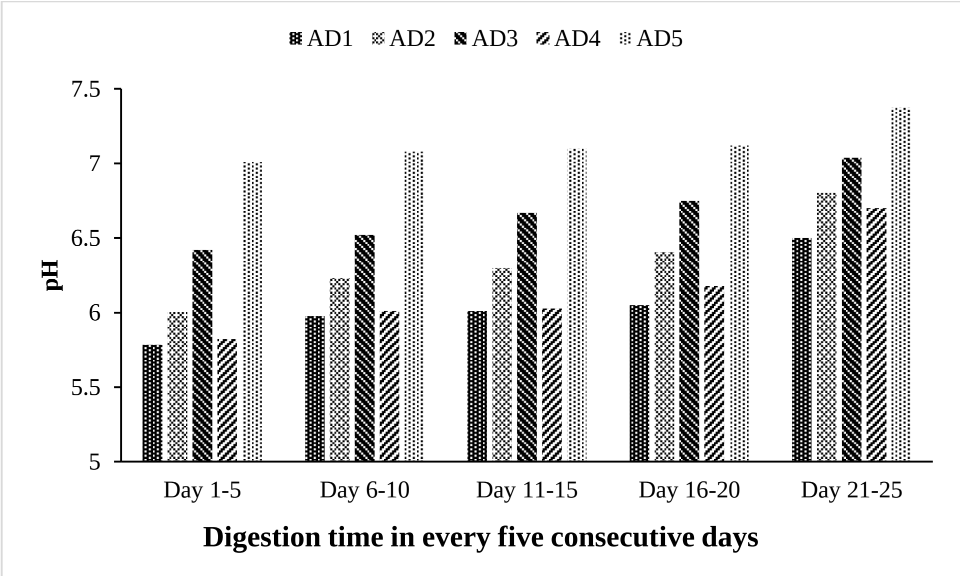

Fig.4 Variation of pH value with digestion time

It can be observed from the figure that, for the digesters AD1, AD2, AD3, AD4, the pH value rapidly decreases at the beginning stages of digestion, as the easily digestible organic matter hydrolyse and further convert to volatile fatty acids. After the initial drop in the pH value, it increases gradually as the volatile fatty acids are consumed by methanogens [33]. Among all the anaerobic digesters AD5 gives a maximum pH. During 2-8 days of the digestion time, a maximum pH value of 6.58 and 6.02 are obtained on 7th and 8th day for the digesters AD2 and AD3 respectively, which is 7.19% and 14.97% less than the digester containing cow manure alone (AD5) respectively. Because of hydrolytic and acetogenic bacterial are observed to be more during those days. During the anaerobic digestion process, the digester AD1, AD2, AD3, AD4, and AD5 shows its peak value on 24th day, 20th day, 22nd day, 21st day, 24th day respectively.

3.2 Effect of C/N

The carbon to nitrogen (C/N) ratio is the most influencing parameter for the biogas production. For an optimum biogas production, it was reported that, the C/N ratio should lie in the range of 20-30:1 [34].

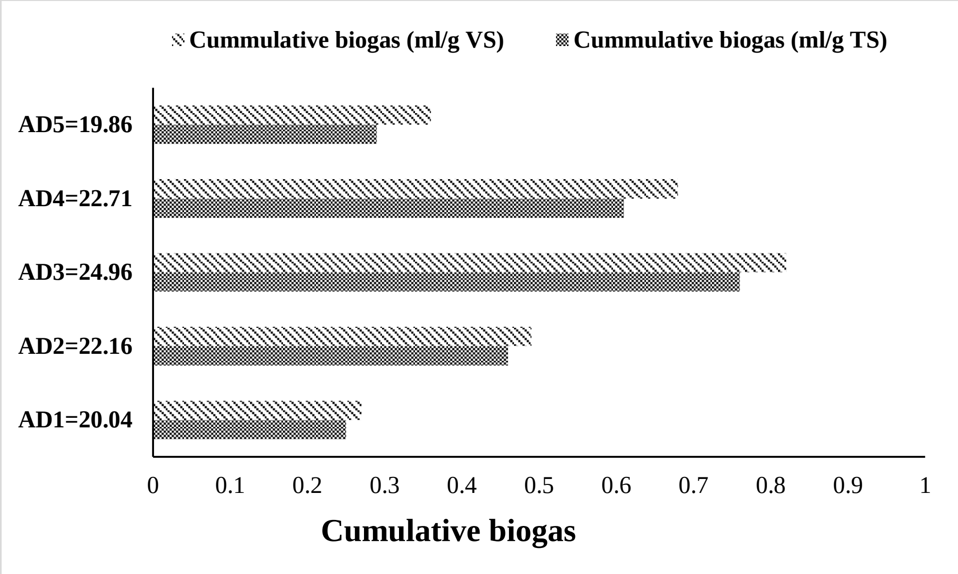

Fig.5 Average cumulative biogas production at different C/N ratios

If the C/N ratio is much higher than the range, then the biogas production will be low. This is because, nitrogen will be consumed rapidly by methanogenic bacteria for meeting their protein requirements, and will no longer react on the left over carbon remaining in the material. If the C/N ratio is very low, that is outside the stated range, nitrogen will be liberated, and it will accumulate in the form of ammonia (NH_3). As a fact, NH_3 will intern increase the pH value of the slurry. A significant amount of release of NH_3 may cause toxic to methanogenic bacteria in the slurry, thus biogas production will be low [35]. Fig.5 depicts the average cumulative biogas production at different C/N ratios for a 25 days of digestion time.

It can be observed from the figure, that the anaerobic digester AD3 gives a maximum biogas production of 0.76ml/g TS (or) 0.82ml/g VS, than AD4 gives 0.61ml/g TS (or) 0.68ml/g VS, than AD2 gives 0.46ml/g TS (or) 0.49 ml/g VS, than AD5 gives 0.29ml/g TS (or) 0.36ml/g VS. It can also be noticed that, the lowest yield for the digester AD1 is 0.25ml/g TS (or) 0.27ml/g VS. The lowest biogas production for AD1 might be due to formation of NH_3, which may lead to toxic to bacteria. It was also reported by the Guermoud et al. [36] and Khalid et al. [37] that, the C/N ratio of 22-25 is the best condition for carrying out anaerobic digestion. The digester AD3 has a C/N ratio of 24.96, which is well under the optimum range. But, on the addition of STW more than 30%, the C/N ratio slightly shifts from the optimum range and tends to decrease. Because of which, excessive nitrogen will be liberated that could inhibit the methanogenic bacteria; thus the biogas production decreases [38].

3.3 Effect of digestion time

Fig.6 depicts the daily biogas production with respect to the digestion time. The average daily biogas production during 25 days of digestion time is observed to be approximately 21.57 ml/day per kg of TS, 40.92 ml/day per kg of TS, 66.77 ml/day per kg of TS, 53.45 ml/day per kg of TS, and 24.67 ml/day per kg of TS for the digesters AD1, AD2, AD3, AD4 and AD5 respectively. It can be observed that, the biogas production in AD1, AD2, and AD5 became stable after 9-10 days of digestion time. It then decreases after 20 days of digestion time, the decrease in biogas production might be due to lack of carbon availability in the digester. Initially, the biogas yield from the digesters AD3 and AD4 is low during 1-5 days of digestion time. It is reported that, when the digestion time is more than 5 days, the methanogenic bacteria will consume volatile fatty acids rapidly, and hence increases the biogas yield [31]. After 5 days, biogas production increases gradually up to 19 days of digestion time, and then biogas production stops, and becomes stable. There is a sudden change in peak of biogas production is observed at 19-22 days of digestion time, because of excessive formation of nitrogen during those days which in turn decreases the C/N ratio and shifts the pH value of the slurry towards alkalinity. Thus a sudden increase and decrease in the biogas production is observed [31]. In this investigation, it is observed that, CM mixed with STW in proportion of 70% and 30% respectively yields 170% more biogas than the sole CM. This may be due to the presence of carbon, nitrogen and organic compounds like $C_6H_{12}O_6$ in the STW. Among all the digesters, AD1 gives the least biogas production.

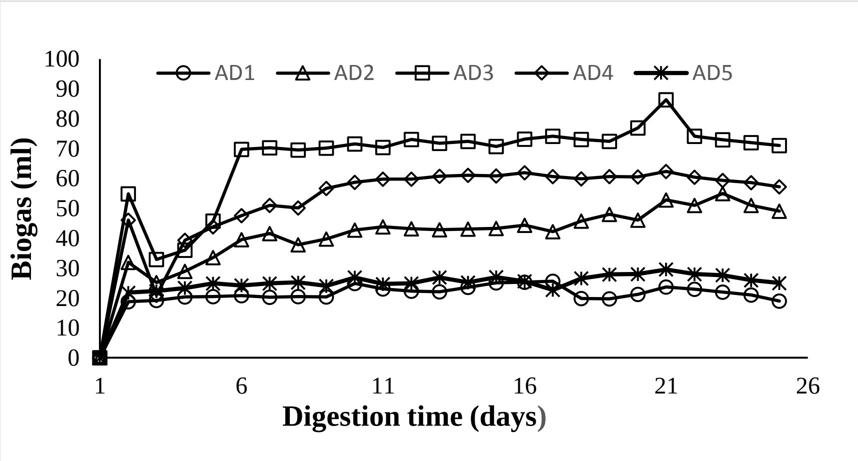

Fig.6 Daily biogas yield in response to digestion time

This is because of the less organic compounds present in the digester for microbial growth and survival.

3.4 Cumulative biogas production

The variation of the cumulative biogas production per unit TS over a 25 days of digestion time for AD1, AD2, AD3, AD4 in comparison with AD5 is shown in Fig.7.

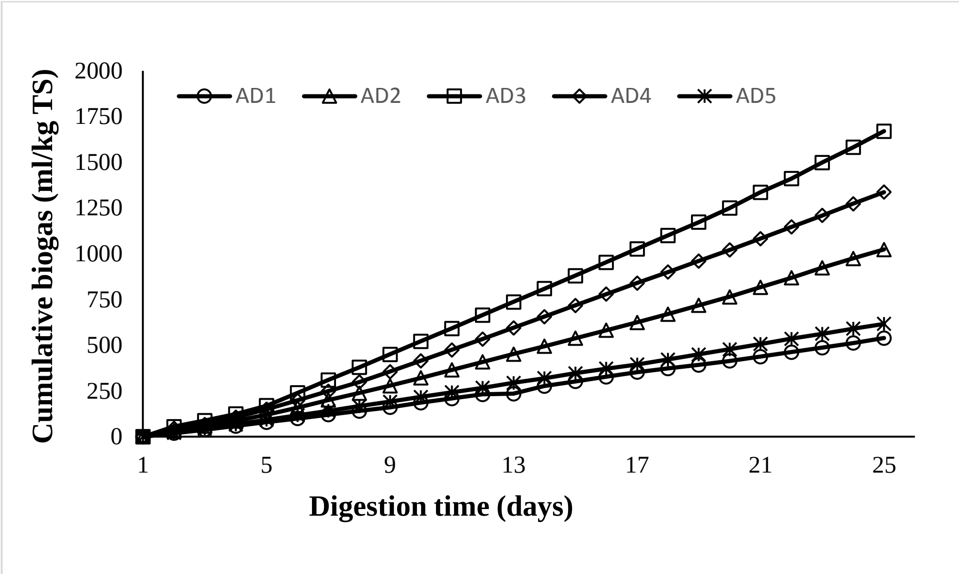

Fig.7 Cumulative biogas yield in response to digestion time

The maximum cumulative biogas production is observed for AD3, followed by AD4. The range of cumulative biogas production for AD3 over a 25 days of digestion time are found to be about 54.92 to 1669.25 ml/kg TS (or) 0.054 ml/g TS to 1.66 ml/g TS and 0.057 to 1.77 ml/g VS. The digester AD3 yields a maximum cumulative biogas of 1669.25 ml/kg TS, which can also be represented as 1.66 ml/g TS (or) 1.77 ml/g VS. The maximum cumulative biogas production for AD3 is observed at an average C/N ratio of 24.96. This might be due to the presence of essential nutrients at correct compositions. In fact, carbon and nitrogen are the main nutrients are the source for a sustainable growth of anaerobic bacteria [31].

3.5 Methane content of the produced biogas

Fig.8 depicts the variation of the methane yield with respect to the digestion time. In this investigation, a similar trend is found for both the biogas production and the methane yield. Although, there ~~was~~ is a huge biogas production in the initial stages of digestion, a little methane is observed during those 4 days. The rapid increase in the biogas production and the low methane content may be due to the presence of some easily digestible organic materials like carbohydrates and rapid acidification of spent tea waste in the digester, which leads to decrease in the methane yield during the early stages of digestion [32]. The dissipation of easily digestible organic materials leads to temporary biogas production. A maximum methane produced from the AD1, AD2, AD3, AD4, and AD5 during first 4 days is 21.18%, 31.92%, 39.97%, 36.42%, and 23.34% which corresponds to 4.31 mlCH_4/kg TS,10.18 mlCH_4/kg TS, 14.40 mlCH_4/kg TS, 7.64 mlCH_4/kg TS, 5.44 mlCH_4/kg TS respectively. Similar results was observed by Mashad and Zhang [28], when they investigated on the production of biogas from co-digestion of dairy manure and food waste. The methane content in the biogas produced from the digesters AD3 and AD4 is 39.97% on 5th day, and 33.54% on 4th day, reaching to continue its increasing trend till 21st day, which is similar to biogas production. The methane yield and biogas production patterns show inhibition of methanogenic bacteria in the first 4 days due to acidification in the digester [39].

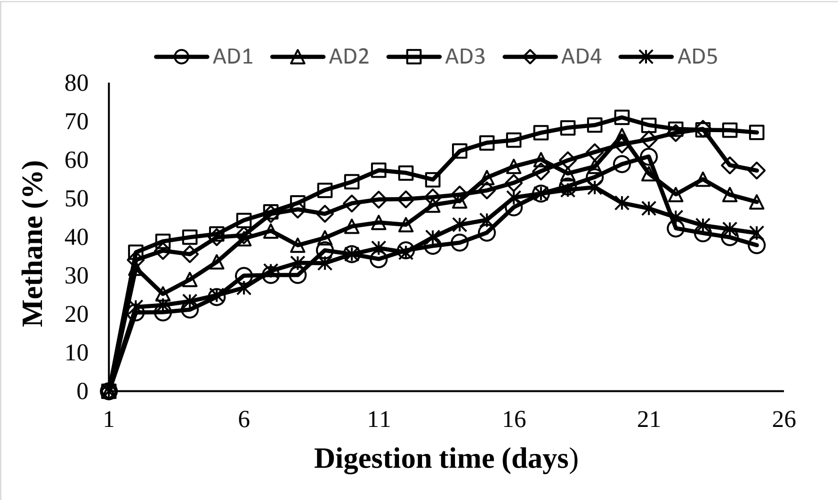

Fig.8 Variation of methane yield with respect to digestion time

As methane (CH_4) is the only useful gas in the biogas, the digester with the highest methane yield is considered as the best combination of substrates. The highest methane percentage is obtained in the AD3 followed by AD4. It can be observed from the figure that, AD5 which contains only cow manure produces lower methane when compared to other digesters. Therefore, it indicates that, co-digestion of CM with STW is an effective approach for methane improvement. Addition of two or more substrates increase the biogas production and the methane yield has been reported previously. Maranon et al. [40] obtained a higher methane yield of 603 mlCH_4/g-VS when co-digested 70% manure with 20% food waste and 10% sewage sludge. In this study, during the final stages of anaerobic digestion of CM with STW, the growth of microbes is reduced, due to the increase in the NH_3 production, resulting in the decrease in the methane yield [41].

3.6 Characterisation of biogas

The biogas obtained from the digesters AD1, AD2, AD3, AD4 and AD5 were characterized for determining its density, temperature, energy content, lower calorific value, boiling point and gas constituents. The properties of the biogas are given in Table 6. The biogas composition (CH_4, CO_2, H_2S, H_2, NH_3, etc.,) were analysed as per the ASTM D 7833 [42]. Biogas constituents of this study were compared with some of the commonly available literature, and are presented in Table 7. It can be inferred that, AD3 shows a high methane content of about 71% which is 16%, 6.28%, and 4.41% more methane obtained from AD1, AD2, and AD4 respectively. AD2 shows a methane content of about 67%. A similar methane composition was reported by Jena et al. using semi dried banana leaves [48], and Rasi et al. digesting sewage sludge [46], however a marginal increase in CO_2 content in banana leaves and sewage digester may decrease the calorific value of methane. It was noticed that, biogas obtained from AD3 had a better quality of biogas than those of other digesters used in this study. A higher methane content (about over 70%) in AD3 indicates a greater tendency to resist knock due to its high octane rating and auto-ignition temperature, when it is used as an alternative gaseous fuel for IC engines, if produced in a large quantity [11]. Also, a large reduction in emissions could be achieved by using biogas as a fuel [49].

Table 6 Properties of biogas obtained from AD1, AD2, AD3, AD4, and AD5

Properties	Test method	AD1	AD2	AD3	AD4	AD5
Density at 1 atm, kg/m^3	D 3588	1.28	1.24	1.18	1.27	1.33
Auto ignition temperature, ^{o}C	-	642-655	620-635	605-640	610-645	650-670
Energy content, kW/m^3	D 4868	3.3-4.1	3.9-4.8	5.1-5.7	4.1-5.2	4-4.5
Lower heating value, MJ/kg	D 1945	19.1	22.1	26.4	24.2	16.1
Boiling point, ^{o}C	D 1835	-128 to -170	-122 to -160	-118 to -152	-113 to -155	-130- to -162

Table 7 Comparison of gas constituents obtained in this study with available literature

Feed stock	Test method D 7833* [42]						
	Gas Constituents						
	CH_4 (%vol.)	CO_2 (%vol.)	H_2S (%vol.)	O_2 (%vol.)	N_2 (%vol.)	H_2 (%vol.)	NH_3 (%vol.)
AD1*	61.2	27.9	0.28	1.52	7.7	0.8	0.6
AD2*	66.8	23.4	0.25	1.35	6.5	0.9	0.8
AD3*	71	18.8	0.18	1.92	5.8	1.2	1.1
AD4*	68	22.7	0.23	1.37	6.4	0.8	0.5
AD5*	50-70	25-30	0-3	0-3	0-10	0-1	0-1
Household waste [43]	50-60	34-38	NF	0-1	0-5	NF	NF
Waste water treatment sludge [43]	60-75	19-33	NF	<0,5	0-1	NF	NF
MSW [43]	40-60	20-40	0.004-0.01	<1	2-20	NF	NF
Cowpea [44]	56.2	33.2	0.5	NF	NF	NF	NF
Cassava peelin [44]	51.4	32.2	3.1	NF	NF	NF	NF
Cow dung [44]	67.9	27.2	0.1	NF	NF	NF	NF
Maize silage [45]	54.77	41.96	289.65 ppm	0.375	NF	NF	NF
Maize silage and grass haylage [45]	53.97	42.64	182.65ppm	0.36	NF	NF	NF
Maize silage, grass haylage, and rye grain [45]	54.37	42.49	175.47 ppm	0.38	NF	NF	NF
Land fill [46]	47-57	37-41	36-115 ppm	<1	<1-17	NF	NF
Sewage digester [46]	61-65	36-38	<0.1 ppm	<1	<2	NF	NF
Agricultural/Animal waste [47]	55-58	37-38	3-1000 ppm	<1	<1-2	NF	NF
Semi dried banana leaves [48]	65.28	31.82	NF	NF	1.27	0.06	NF

*- Data obtained in this study
NF- Not found

3.7 Characterisation of slurry

In contrast to direct combustion, pyrolysis and gasification, anaerobic digestion produces both fuel and a bio-digested slurry called digestate [50]. The digestate exiting the biogas digester is rich in both macro and micro-nutrients. When it is used in land it enhances the physical, chemical and biological attributes of the soil, as of original manure [51]. Therefore, the bio-digestate slurry can be used as a fertilizer. In general, the digestate contains N_2 (1.8%), P (1.0%), and K (0.9%) [52]. The N, P, and K values of the present study are compared with some of the literature results and are shown in Table 8. It can be observed from the table that, the bio-digested slurry consists of comparable amount of organic matter as well as macro-nutrients (N, P and K). Furthermore, the macro-nutrients concentration of AD3 is significantly higher than the FYM [52], vermicompost [52], chicken manure [53], and Rabbit manure [53]. It can also be inferred from the table that, among the samples conducted in this study, AD3 showed its highest N, P, K values followed by AD2, and AD1. The presence of nitrogen fixing and phosphate solubilizing organisms in the digestate shows that, the digestate ~~it~~ could be utilized as an efficient bio-fertilizer for the growth of crops [54]. Also, it is noticed that, after anaerobic digestion the concentration of N, P, and K increased. This might be due to action of micro-organisms which significantly reduces the microbial pathogens. Hence, it is a good sign for the growth of plants [54]. A similar kind of results were obtained by Owamah et al. [55] from the co-digestion of food waste and human excreta. From these experimental results, it is suggested that, the bio-digested slurry from co-digesting CM and STW can be used as an organic fertilizer. Therefore, the problem associated with the disposal of STW can be minimised.

Table 8 Fertilizer value of bio-digested CM-STW slurry of all digesters

Digester name	Carbon, %	Nitrogen (N), %	Potassium (K), %	Phosphorous (P), %	N/K-ratio	N/P-ratio
AD1	56	4.9	2.8	1.8	1.75	2.72
AD2	53	5.5	3.3	2.3	1.66	2.39
AD3	49	6.7	3.7	2.9	1.81	2.31
AD4	45	3.8	2.5	1.7	1.52	2.23
AD5	38	2.7	2.1	1.2	1.28	2.25
Farm yard manure [52]	25-55	0.4-0.8	0.6-0.82	0.5-0.65	NF	NF
Vermicompost [52]	9.8-13.4	0.51-1.61	0.19-1.02	0.15-0.73	NF	NF
Horse manure [53]	NF	0.7	0.6	0.3	1.16	2.33
Chicken manure [53]	NF	1.1	0.5	0.8	2.2	1.37
Sheep manure [53]	NF	0.7	0.9	0.3	0.77	2.33
Rabbit manure [53]	NF	2.4	0.6	1.4	4	1.71
Pig manure [53]	NF	0.8	0.5	0.7	1.6	1.14
Food waste with human excreta [55]	20.1 ± 0.44	0.7 ± 0.03	NF	NF	NF	NF

NF- Not found

4 Conclusions

An experimental investigation was carried out to assess the possibility of using spent tea waste (STW) for its energy use. For biogas production, STW was co-digested with CM, and the performance is assessed by considering the input parameters like pH, C/N, and digestion time. The following points are the conclusion of the investigation;

- STW a solid organic waste obtained as a municipal as well as a food waste can be co-digested with cow manure for obtaining biogas containing a maximum methane content of about 70%.

- A maximum biogas production can be obtained from the co-digestion of substrate containing 30% STW and 70% CM, for a digestion time of 25 days.

- AD3 shows a max pH value of 7.16, which indicates good for anaerobic digestion. The biogas obtained from the digester AD3 has a heating value and energy content of 26.4 MJ/kg and 5.1-5.7 kW/m^3 respectively.

- The fertilizer values of AD2, AD3, and AD4 holds good for growth of plants than other digesters.

- Further, investigations may be carried out at different operating conditions (organic loading rate (OLR), temperature, etc., and at different reactors (continuous and fed-batch systems), which is not considered in this study), to show its potential for usage in industrial applications.

- More possibilities can be explored on co-digestion of STW with multiple organic wastes that originate from agriculture, municipal and industrial wastes for producing a large quantity of biogas at a single point. Assessment of pre-treatment of STW can be carried out for ensuring the quality and yield.

- Finally, possibilities of long-term field research based on a comprehensive approach including storage, handling and application of both animal manure and bio slurry as fertiliser and soil improver may be explored.

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