

BIOMETHANIZATION POTENTIAL OF WASTE AGRICULTURAL BIOMASS IN PAKISTAN: A CASE STUDY

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Abstract

Waste agricultural biomass (WAB) can be used as source of energy for domestic and industrial applications. In the light of this vision nine WAB samples were collected from district Sanghar and processed as per standard methods and analyzed for moisture content, total solids, volatile solids by thermo-gravimetric analysis (TGA). In addition to this ultimate analysis was also carried out. The theoretical methane potential of WAB in district Sanghar was estimated as 535976 km³/y. The experimental methane potential was estimated as 197284 km³/y, which is about 37 % of the theoretical methane potential. The results indicate that WAB has significant energy potential in terms of methane, which can be utilized for cooking, heating and power generation purposes.

Keywords : Waste Agricultural Biomass, Methane Potential, Thermo Gravimetric Analysis, Anaerobic Digestion.

1. Introduction

Waste agricultural biomass (WAB) is an agricultural residue, assorted as field residues, which is the matter leftover in an agricultural field after the crop has been reaped and the process residues, which are the matter leftover after the processing of the crop at the mills into a valuable products. Their characterization is really significant from the energy conversion process standpoint. At present WAB is one of the feasible solutions, to meet the increasing energy needs without compromising the environment. Pakistan nowadays is having an energy crisis. In order to fulfil the energy demand, the exploitation of all renewable energy resources is very much necessary.

Biomass can be converted into a variety of energy forms including heat (direct burning), electricity (steam and gasification), hydrogen, ethanol, methanol, and methane. Selection of a product for conversion depends upon a number of factors including need for direct heat or steam, conversion efficiencies, energy transport, type of technology, economics, and environmental impact of conversion process waste streams and product use. In most circumstances methane is an ideal fuel [1]. The anaerobic digestion is the biochemical process by which biodegradable organic matter can be converted into methane. Anaerobic digestion is largely applied today to produce biogas in airproof reactor tanks, commonly named as digesters. A wide range of micro-organisms are involved in the anaerobic process which has two main end products; biogas and digestate. Biogas is a combustible gas consisting of methane, carbon dioxide and small amount of other gases like hydrogen sulfide, nitrogen, hydrogen and carbon monoxide [2]. Methane

produced during the anaerobic digestion process comprises of about 50 to 65 % of the biogas. Methane is a colorless, odorless and flammable gas with an energy value of 37.3 MJ/m³ [3]. Digestate is the decomposed substrate being rich in macro- and micro nutrients can be suitable for the use of organic fertilizer [4].

The generation and utilization of biogas provide environmental and socio-economic benefits for the society as a whole. Biogas can be utilized for various purposes. The simplest application of biogas is its direct use for cooking and lighting. Biogas can also be used for combined heat and power generation (CHP). On the other hand the generation of the biogas and digested substrate from AD creates new jobs related to the collection and transport of feedstock, manufacture of biogas plant equipments, construction, operation and maintenance of biogas plants etc. [4].

Pakistan is an agrarian country and produces huge amount of crops, such as rice, sugarcane, cotton, wheat, maize, bajra, jowar, gram, tobacco, rapeseed, barley and mustard annually. These crops also generate large quantity of residues every year. These residues constitute a major part of the total annual production of biomass residues and are important sources of energy for both domestic as well as industrial purposes. In Pakistan, there are many domestic biogas plants in operation but their feedstock is the dung of cows and buffalos. In developed countries, there is good number of commercial as well as farm scale biogas plants in operation with a feedstock of animals dung and WAB. But in Pakistan there is no any practice of using the co-digestion of WAB with animal dung.

According to the field survey of WAB in district Sanghar, huge quantity of WAB is wasted [5]. In order to highlight the benefits of the biogas from WAB and its potential in Pakistan this analytical study has been carried out for the first time.

2. Methodology

2.1. Study Area

The area selected for case study was Sanghar district, which is one of the largest districts of the province of Sindh, Pakistan. The district Sanghar lies between 25° to 30° North latitudes and 70° to 13° East longitudes. The total area of the district is about 987313 ha. It is primarily an agricultural district where wheat, cotton, sugarcane and rice are being grown in a substantial quantity. Moreover, canola, millet, barley, groundnuts, vegetables, pulses, maize, banana and many other crops are also grown there. The population of the district is about two millions. The district Sanghar is administratively divided into six subdivisions: these are Sanghar, Sinjhor, Shahdadpur, Tando Adam, Jam Nawaz Ali, and Khipro. Administratively each subdivision is further divided into union councils. Total number of union councils in the district Sanghar is 59 [6].

2.2. Preparation Of Samples For Analysis

Total nine agricultural residue samples were collected from the field i.e. banana plant waste, canola straw, cotton stalks, rice straw, sugarcane tops, wheat straw, bagasse, cotton gin waste and rice husk. These were selected on the basis of their availability in substantial quantity and from energy conversion point of view. To obtain the representative sample, samples were dried at room temperature, then ground into the powder form and then sieved through a 250 µm sieve [7].

2.3. Moisture, Total Solids, Volatile Solids And Ash Of WAB

Moisture content (MC) in WAB is the measurement of the loss of weight due to drying at a temperature of 105 °C. The total solids (TS) were calculated by subtracting moisture from hundred percent. The weight loss on ignition at 550 °C is an approximate measure of the organic matter content in the WAB also known as volatile solids (VS), where as the residue left after combustion of the oven dried WAB is a measure of total mineral content and also called ash [7,8]. All the three parameters stated above for selected residues of WAB were determined by using a thermo gravimetric analyzer (TGA model SDT-Q600) as per ASTM standard method E1131-08 [9]. According to this method WAB samples were taken in the range of 15 to 30 mg and run in duplicate.

2.3.1. TGA Test Procedure

After charging the samples into the analyzer the test procedure was specified. The test procedure was the description of the segments, which were carried out during the test. The segments described that, first the temperature of the furnace of the instrument was increased up to 105 °C at the rate of 20 °C per minute. Then after holding this temperature, the isothermal condition was maintained for 15 minutes. This results the loss of weight of the sample, which is the measure of the moisture of the sample. Then the temperature of the furnace was increased in inert atmosphere of nitrogen up to 550 °C at the rate of 45 °C per minute and held for a short time to stabilize the loss of weight, resultantly loss of weight of sample was obtained.

Afterwards the nitrogen gas was changed to oxygen in order to ignite the sample and the isothermal condition was maintained at 550 °C for 10 minutes. This results further more loss of weight of the sample. Finally at the end of the cycle, the sample remained in the pan was ash, where the total weight loss occurred except moisture and ash was the organic matter present in the sample.

2.3.2. Analyzing The TGA Output

The output of the simultaneous TGA/DSC analyzer is in the form of graphs. The default output graph is between the temperature of the furnace in degrees Celsius and the weight loss in percentage as shown in Figs. 1 and 2. The exact values of the moisture content and the ash were extracted from the graphs by using the TA Instruments' built-in software. The name of the software is Universal Analysis 2000. Two tests were performed for each sample of the WAB and then the average was taken for the final result.

2.4. Ultimate Analysis

The standard procedure according to ASTM D3176 method was used for the ultimate analysis [10]. The percentage of carbon, hydrogen, nitrogen and sulfur were determined by using vario MAX elementary analyzer for all the nine selected residues of the waste agricultural biomass. Oxygen content was calculated by subtracting percentages of carbon, hydrogen, nitrogen, sulfur and ash from hundred percent. Moreover, the percentages of the hydrogen and oxygen were corrected by using the moisture content of the WAB samples. The results of the ultimate analysis of the WAB samples with the adjustment of the moisture content are given in Table 1.

Table 1 : Results Of Ultimate Analysis Of WAB

Sample No	Name of WAB	C	H	O	N	S	Ash
1	Bagasse	44.65	5.54	44.91	0.18	0	4.72
2	Banana Plant	38.31	5.35	39.15	0.39	0.1	16.71
3	Canola	39.66	5.32	44.35	0.2	0.93	9.54
4	Cotton Gin Waste	39.87	5.06	32.01	1.7	0.6	20.77
5	Cotton Stalks	42.84	5.63	41.05	0.08	0.42	9.98
6	Rice Husk	36.85	5.55	35.1	1.7	0.22	20.58
7	Rice Straw	36.39	4.96	38.68	1.01	0.22	18.75
8	Sugarcane Tops	39.92	3.72	42.46	0.15	0.14	13.62
9	Wheat Straw	40.83	5.34	38.13	0.83	0.24	14.64

2.5. Quantity Of WAB

The quantity of the each crop residue in each subdivision was calculated by using Eq. 1;

$$AQPY = AAC \times CY \times YRR \times AF \quad (1)$$

where AQPY is available quantity of WAB per year (t/y), AAC is annual area cultivated (ha), CY is crop yield (t/ha), YRR is yield to residue ratio and AF is the availability factor of crop. The annual area cultivated for each of the crop in each subdivision of Sanghar was taken from the data, which is provided by the Crop Reporting Services, Pakistan. The crop yield, yield to residue ratio and the availability factor of each crop in each subdivision were taken from the results of the field survey conducted in district Sanghar [5]. The total quantity of WAB (TQ) for each subdivision is given in Table 2.

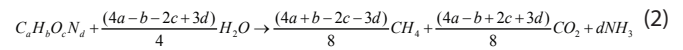
Table 2. Available Quantity Of WAB In District Sanghar [5]

S No	Name of WAB	AQPY (t/y)						
		Sanghar	Sirjoro	Shahdadpur	Tando Adam	Jam Nawaz Ali	Khipro	TQ
1	Bagasse	1670	1443	955	1146	434	544	6193
2	Banana Plant	1415	4619	28210	48814	2092	1777	86927
3	Canola Straw	5315	2665	2620	2176	734	1498	15008
4	Cotton Gin Waste	10313	14319	14182	5750	5152	14326	64041
5	Cotton Stalks	57294	143187	157572	89445	91584	206931	746014
6	Rice Husk	1683	4588	640	985	1514	2122	11531
7	Rice Straw	5923	15141	1972	3249	4995	7468	38748
8	Sugarcane Tops	68163	47133	31198	37416	14183	17776	215869
9	Wheat Straw	36584	82460	51225	31720	17769	38105	257863
	TOTAL	188359	315555	288574	220701	138457	290548	1442194

2.6. Theoretical Methane Potential Of WAB

The theoretical amount of methane gas can be estimated using the

ultimate analysis of WAB by using Eq. 2 [8]. It represents the general anaerobic transformation of organic waste, assuming that the organic waste stabilized completely. The term $C_a H_b O_c N_d$ represents (on molar basis) the composition of the organic material present at the start of the process.



First by using the ultimate analysis of WAB the molar concentration of the elements were estimated by neglecting the ash content, then the approximate chemical formula of the each WAB was determined by considering the nitrogen mole ratio as one. The derived coefficients of empirical formulae were used in Eq. 3 to estimate the specific methane theoretical (SMT) in m^3/t . The density of methane was taken as 0.7167 kg/m^3 at standard temperature and pressure [8]. The methane potential theoretical (MP_T) was estimated by multiplying total quantity (TQ) of WAB with SM_T . TQ of WAB in each taluka of district Sanghar is given in Table 2.

$$SM_T = \frac{\frac{(4a + b - 2c - 3d)}{8} \times \text{molar mass of } CH_4 \times \%TS(1 - \%Ash) \times 1000}{C_a H_b O_c N_d \times \text{density of } CH_4} \quad (3)$$

2.7. Experimental Methane Potential Of WAB

Different researchers have worked on the methane production from the WAB at the laboratory scale. This could be termed as specific methane experimental (SM_E). SM_E obtained from the literature review is given in Section 3.3. The amount of methane was reported either in terms of total quantity (TQ) of WAB as in case of cotton stalks and cotton gin waste or in terms of total solid (TS) of WAB as in case of banana plant or in terms of volatile solids (VS) in the literature. To make the uniformity, all values of SM_E were converted in terms of TQ. Then methane potential experimental (MP_E) was estimated by multiplying TQ of WAB with SM_E .

3. Results & Discussion

3.1. Results of TGA analysis

The TGA result of first sample of banana plant is shown in Fig. 1. On abscissa, it represents temperature in degree Celsius ($^{\circ}C$); whereas ordinate represents weight of the sample in terms of percentage. It can be observed from the Fig. 1 that, the moisture content of the sample is 4.76 %, volatile solids are 78 % and the ash is 17.24 %.

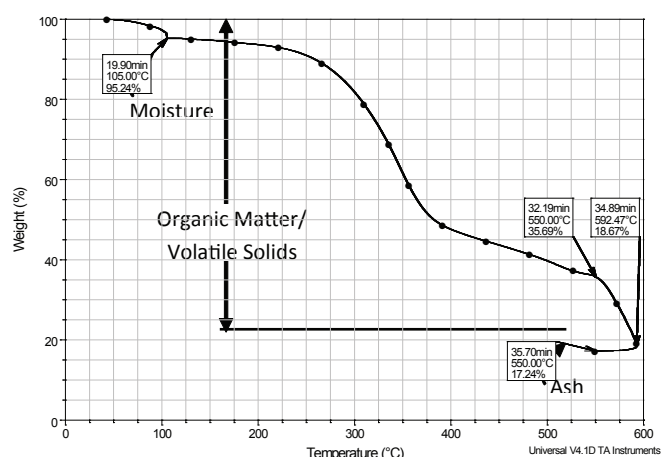


Figure 1 : TGA Graphical Result Of Banana Plant Sample # A

Similarly the TGA result of the second sample of the banana plant is shown in Fig. 2. The results of moisture, VS and ash are extracted from the figure as 7.17 %, 76.66 % and 16.17 % respectively.

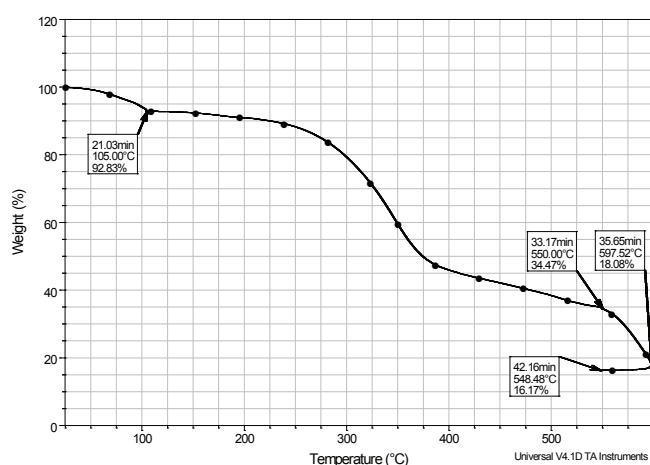


Figure 2 : TGA Graphical Result Of Banana Plant Sample # B

The TGA results of other samples were extracted from their respective graphs similarly and average results are given in Table 3.

Table 3 : Average Results Of TGA Analysis For WAB Samples

Sample No	Name of WAB	MC	TS (%)	% VS	VS (%)	Ash (%)
		(%)		in TS		
1	Bagasse	3.11	96.89	95.13	92.17	4.72
2	Banana Plant	5.97	94.04	82.24	77.34	16.71
3	Canola	9.09	90.92	89.51	81.38	9.54
4	Cotton Gin Waste	4.55	95.45	78.24	74.68	20.77
5	Cotton Stalks	4.85	95.15	89.51	85.17	9.98
6	Rice Husk	4.8	95.2	78.38	74.62	20.58
7	Rice Straw	3.33	96.68	80.61	77.93	18.75
8	Sugarcane Tops	2.43	97.57	86.05	83.96	13.62
9	Wheat Straw	4.33	95.68	84.7	81.04	14.64
MC = Moisture Content, VS = Volatile Solids, TS = Total Solids						

3.2. Results Of Theoretical Methane Potential

The results of the SM_T of WAB in terms of TQ are given in Table 4, along with the coefficients of empirical formula. By using SM_T results, MP_T for the district Sanghar was estimated and is given as $535976 \text{ km}^3/\text{y}$.

Table 4 : Results Of SM_T And MP_T Of WAB

S No	Name of WAB	Coefficients of empirical formula (Eq. 2)				SM_T (m^3/t)	MP_T (km^3/y)
		a	b	c	d		
1	Bagasse	289	427	218	1	398	2467
2	Banana Plant	115	190	88	1	344	29927
3	Canola Straw	231	369	194	1	331	4967
4	Cotton Gin Waste	27	41	17	1	374	23965
5	Cotton Stalks	625	976	449	1	393	292972
6	Rice Husk	25	45	18	1	347	4006
7	Rice Straw	42	68	34	1	325	12581
8	Sugarcane Tops	310	344	248	1	318	68653
9	Wheat Straw	57	89	40	1	374	96438
Total MP_T of WAB of district Sanghar							535976

3.3. Results Of Experimental Methane Potential

The SM_E of WAB for its each type is given in Table 5, along with the references. By using SM_E results, MP_E for the district Sanghar was estimated and is given as $197284 \text{ km}^3/\text{y}$.

Table 5 : Results Of SM_E And MP_E Of WAB

Sample No	Name of WAB	Methane (m^3/t) on the basis of TQ/TS/VS;		HRT (days)	Reference	Correction factor	SM_E (m^3/t)	MP_E (km^3/y)
		SM_E'				SM_E/SM_E'		
1	Bagasse	144	TS	30	[11]	0.969	140	864
2	Banana Plant	196	TS	25	[12]	0.94	184	16021
3	Canola Straw	290	VS	N. A.	[13]	0.895	260	3895
4	Cotton Gin Waste	87	TQ	28	[14]	1	87	5572
5	Cotton Stalks	65	TQ	23	[15]	1	65	48491
6	Rice husk	367	VS	N. A.	*	0.784	288	3318
7	Rice Straw	367	VS	12	[16]	0.806	296	11462
8	Sugarcane Tops	200	TS	30	[11]	0.976	195	42138
9	Wheat straw	300	VS	N. A.	[17]	0.847	254	65523
Total MP_E of WAB of district Sanghar								197284
TQ = Total Quantity, TS = Total Solids, VS = Volatile Solids in % TS								
* Assuming methane generation equal to Rice Straw								

3.4. Discussions

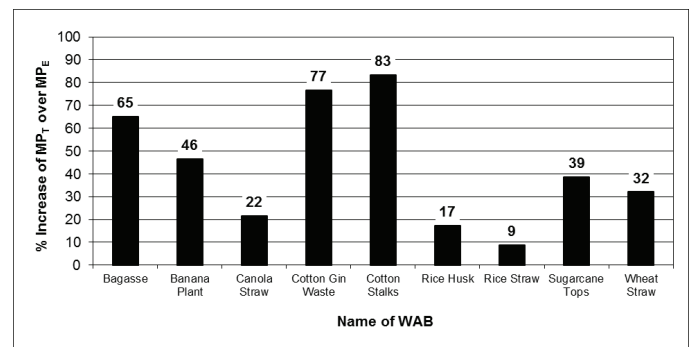
Through the TGA analysis moisture, TS, VS and ash content were obtained. The moisture in all WAB samples was observed in the range of 2-9 %. The minimum and maximum moisture was observed in sugarcane tops and canola straw respectively. The VS in all WAB samples were observed in the range of 75-92 %. The minimum VS was observed in rice husk and maximum in bagasse. Similarly minimum carbon content was observed in rice straw and rice husk about 37 % and maximum in bagasse about 45 %. This indicates strong correlation between VS and carbon content, that higher the carbon content, higher the VS. The results of the ultimate analysis are comparable with the literature [18-23].

The maximum and minimum SM_T were observed in bagasse 398 m^3/t and in sugarcane tops 318 m^3/t respectively whereas the maximum and minimum SM_E were obtained in rice straw 296 m^3/t and 65 m^3/t in cotton stalks respectively. This indicates very high variation in the SM_T and SM_E . The SM_E of rice straw was high because it was pretreated with acetic–propionic acid [16], whereas the SM_E of cotton stalks was low because it was untreated. Moreover the biodegradability of the lignocellulosic biomass highly depends upon the percentage of the lignin content, higher the lignin content, lower will be the biodegradability [8].

The total MP_T for the district Sanghar is estimated as 535976 km^3/y and the total MP_E is estimated as 197284 km^3/y which is only 37 % of the MP_T and is equivalent to 7.36 TJ/y of heat energy. If we convert it into the electricity, then considering 30 % overall efficiency 613223 kWh of electricity per year can be generated.

The increase in MP_T over MP_E is shown in Fig. 3. MP_T of rice straw is only 11 % greater than the MP_E which shows that rice straw has more readily degradable organic matters and during anaerobic decomposition easily converted in biogas. In contrast MP_T of

cotton gin waste, cotton stalks, and bagasse is 50 % more than MP_E which shows that these residues are slowly degradable. Silverstein et al. [24] reported that cotton stalk fibers have lower cellulose and ash but higher lignin content of about 30.1 %. Gupta [25] determined the lignin content of 22.4 % in cotton gin waste, and the lignin content in bagasse was as high as 25.5 % [26]. The MP_T of canola straw, rice husk, sugarcane tops, banana plant and wheat straw is in the range of 20-50 % over MP_E which indicates that these residues are moderately degradable.

**Figure 3** : Percentage Increase Of MP_T Over MP_E Of WAB

4. Conclusions

The experimental methane potential was taken from the literature. The theoretical methane that could be produced from the district Sanghar's WAB is 535976 km^3/y , whereas the experimental methane is about 197284 km^3/y , which is only 37 % of the theoretical methane potential and is equivalent to 7.36 TJ/year of heat energy. If we convert it into the electricity, then considering 30% overall efficiency we can generate 613223 kWh of electricity per year.

Moreover the percentage increase in MP_T over MP_E in WAB was observed low in rice straw about 11 % and high in cotton stalks about 84 %. It not only depends upon the volatile solids but also on the lignin content, which influences the biodegradability. This also indicates that volatile solids of rice straw are easily degradable which can be fermented during the hydraulic retention time (HRT) in the anaerobic digestion. However volatile solids of cotton stalk are slowly degradable and cannot be degraded during the HRT in the anaerobic digestion. The MP_T of canola straw, rice husk, sugarcane tops, banana plant and wheat straw is in the range of 20-50 % more than MP_E . Volatile solids of these WAB residues are moderately degradable. For those WAB residues, their MP_T over MP_E is not more than 50 %, therefore it can be suitable for methane generation.

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