Comparative Study of Enriched Biogas Bottling Cylinder in the Presence of Distinct Filler at Low Pressure

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Sameer Ahmad Khan[1,*], Komalkant Adlak[1], Ujjiban Kakati[1], Ram Chandra[1], Virendra Kumar Vijay[1]

[1]Centre for Rural Development and Technology, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India.
Sameer Ahmad Khan, 8755929917, sksam786@gmail.com
Komal Kant Adlak, 8718012975, komalkant30@gmail.com
Ujjiban Kakati, 8892705912, ujjibankakati@gmil.com
Ram Chandra, rchandra@rdat.iitd.ac.in
Virendra Kumar Vijay, vkvijay@rdat.iitd.ac.in

Abstract

Biogas production is a very retro technology that requires some technological advancement in order to compete with the recent fuel demand. Only biogas is not sufficient it has to be enriched before applying it to recent applications, i.e., mobile and stationary. In stationary applications mainly household or domestic fuel requirement is focussed. Low-pressure high-volume storage of enriched biogas is such an advancement in the biogas sector. Enriched biogas can be compressed under high pressure (200 bar) in order to increase the storage capacity or increase the energy density. To make it fit for domestic usage the enriched biogas must be bottled at low pressure (20 bar). Our work shows a possibility in the same direction, i.e, storing the enriched biogas at low pressures. The appropriate experiments were performed on the storage cylinder in two ways, one is simple compression and in another method, the cylinder was filled with adsorbing material (activated carbons produced from biomass). Three different materials, i.e., activated biochar derived from coconut shell procured from NORIT Americas Inc., pigeon pea stalk biochar, and bamboo biochar developed within the lab at 500 ^{0}C temperature in an inert environment, were used as filler for the bottling cylinder. The desired characterization of raw material and biochar was also performed. Permissible results are found during this study showing that activated biochar is best suited as filler for bottling cylinders to store the enriched biogas.

Keywords: Enriched biogas, Biochar, Pyrolysis, Thermogravimetric analysis, and Adsorbed biogas cylinder (ABG)

*Corresponding Author: rdz188645@iitd.ac.in, sksam786@gmail.com (Sameer Ahmad Khan)

1. Introduction

Biochar is a product produced from pyrolysis of organic matter with presence of high amount of carbon that can be used as adsorbent (Cha et al., 2016). Bio char based on agricultural/forest residue can be produced to work as an adsorbent. Pigeon pea stalk is one such Agricultural residue. Pigeon pea (Cajanus cajan L.) also known as Arhar in local language of India. Pigeon pea stalk could be one such Agricultural residue. India accounts for about 90% of the world supply of pigeon pea. In Asia, pigeon pea is grown in an area of 4.3 million hectare (M Ha) out of which India has the largest area of 3.6 m ha, that produces 3.3 million tons pigeon pea in a year.(" ICRISAT Crops : PigeonPea,"). One hectare of land under production of pigeon pea produces 50-60 quintal(q) of fuel stick or agricultural residue("Pigeon pea — Vikaspedia,"). This results in production of large quantity of feedstock for biochar. Another feedstock for biochar is from forest residue i.e., Bamboo. Bamboo forest spread over 36 MHa Globally, which is about 0.92 % of the world forest area. India is the second major bamboo producing country with 16 MHa (22.46 %) of a total forest area out of a total of 71.2 MHa. Bamboo is a cheap, renewable abundant resource that outgrow most of the plants (Sawarkar et al., 2020). Each biomass is usable for production of biochar. Biochar produced can be used for various application one such application is storage of enriched biogas or biomethane through adsorption.

Physical adsorption is where a molecule known as adsorbate adhere to the surface of other atom also known as adsorbent, with weak van der Waals forces (Suzukl, 1990). In gas adsorption process, the gas molecule is adsorbed on the surface of the microporous material. When raw biogas is processed through any enrichment process the biogas obtained has more methane percentage than the biogas used as feed known as Enriched biogas(Kapoor et al., 2019). According to indian standard when methane percentage in enriched biogas reaches upto a minimum of 90% v/v it is known as biomethane (IS 16087 (2013): Biogas (Biomethane) - Specification [PCD 3: Petroleum, 2013). The energy density of biomethane is low, to increase the energy density of biomethane it can be either transformed to compressed biogas/compressed biomethane (CBG) or liquefied biogas/liquified biomethane (LBG). Another way to increase the Energy density of biomethane is by Adsorption process and this type of biomethane is also called as Adsorbed biogas/ Adsorbed Biomethane (ABG). In an ABG system, Biomethane is adsorbed on activated charcoal, which is packed in the storage vessel, to achieve the desired energy density. ABG has the potential to replace compressed natural gas both in mobile and stationary application. In this adsorption of enriched biogas was studied on biochar produced through bamboo and pigeon pea stalk. Obtained results were compared to ABG system filled with commercially available activated coconut biochar (Khan et al., 2021).

2. Material and Methods

2.1 Sample Preparation

Pigeon pea was bought from rural region of Uttar Pradesh where as bamboo was received from Gramoday Parisar part of IIT-Delhi. Sample preparation for proximate analysis on as received basis of each feedstock was done by removing the dirt as much as possible and cut down to small pieces and then it was powdered, whereas for dry basis, powdered sample was dried for 2-4 hr at 105^0 C in a hot air oven. This powdered sample was also used for CHN (Carbon hydrogen and nitrogen) Analysis, SEM, Thermal gravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR). Small pieces of sample of pigeon pea stalk and bamboo char was prepared by increasing its surface area as much as possible. Sample was powdered using Mixer of 750W. The powdered sample was washed one time with distilled water and dried for 12 hours at 105^0C. FTIR, Iodine number and BET test of biochar sample were also performed. Granular coconut biochar was brought from Norit Americas Inc., which was steam activated. Maximum size of granule was in between 0.42 – 2 mm. Coconut biochar sample was powered and dried for its characterization.

2.2 Biochar Preparation

Sample for pyrolysis was prepared, first by removing the dirt. Then pieces of pigeon pea stalk and bamboo were cut down to approximately 10cm in length. After cutting, these pieces were washed with distilled water and dried for 12hr at 105^0C in hot air oven. Biochar was prepared from dried sample by slow pyrolysis. Nitrogen gas was introduced in the furnace half hour before starting the pyrolysis with help nitrogen cylinder connected to the furnace as shown in figure 1. Sample was pyrolyzed in presence of nitrogen gas at an average heating rate of 10^0C/min at a peak temperature of 500^0C with a residence time of 2 hrs. Biochar obtained was crushed manually to reduce the size. Maximu percentage of biochar have size less 10 mm.

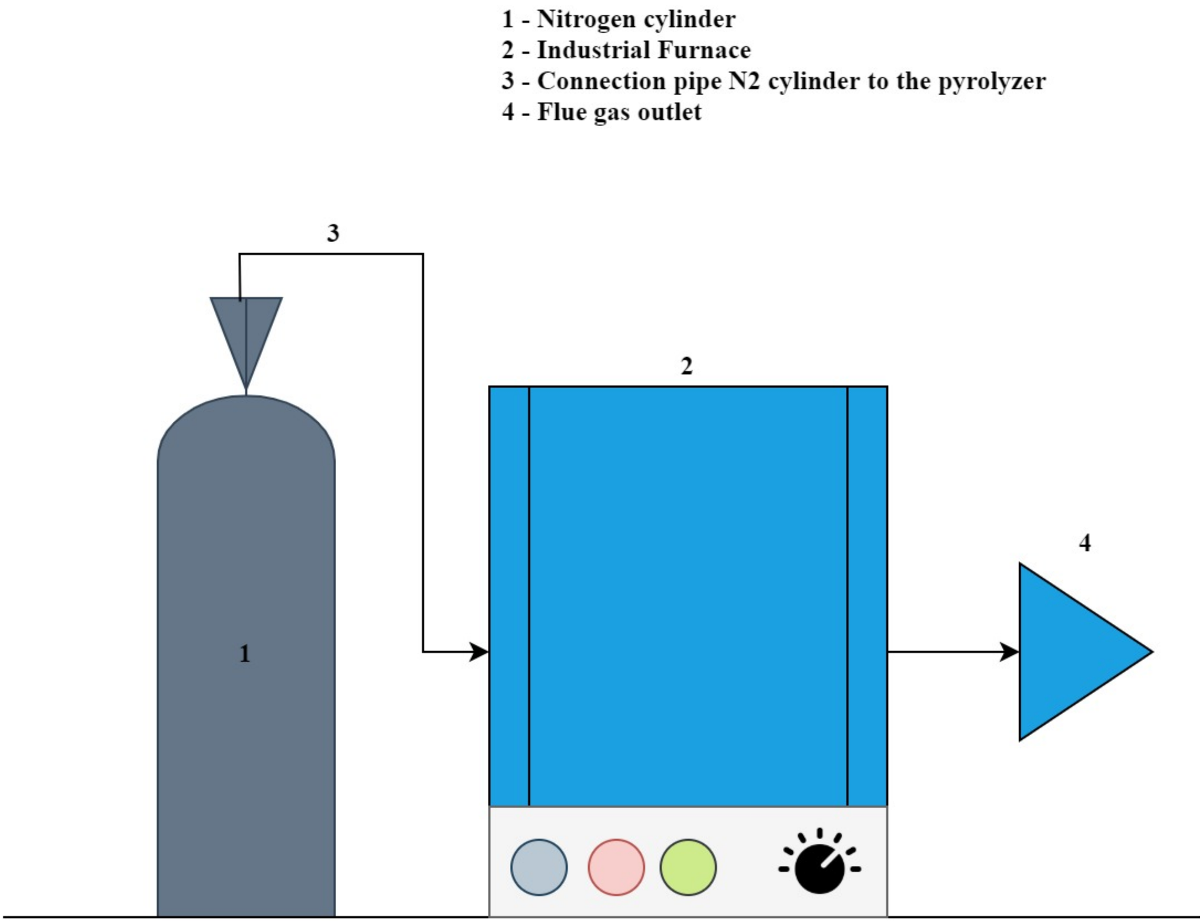


Figure 1. Biochar Production setup (@500^0 C, 10C/min, 2h)

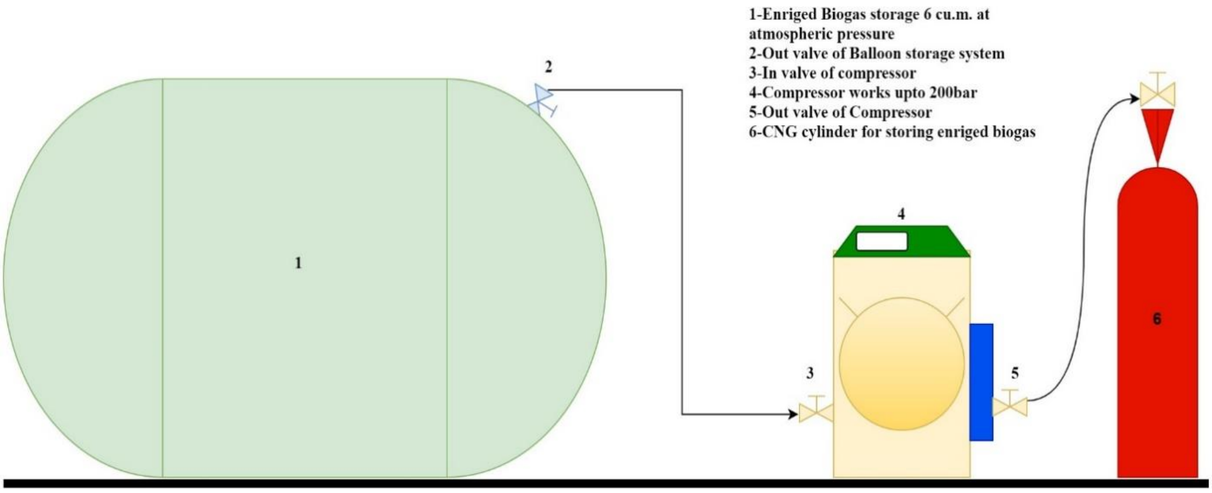
2.3 Sample Characterization

Proximate Analysis of each feedstock was performed on as received basis and on dry basis, for ash content ASTM D1102 − 84(2013) was preferred, moisture content was found with the help of ASTM E871 – 82(2013), Volatile matter follows ASTM E872 − 82(2006) and proximate analysis of biochar was conducted according to ASTM D1762 - 84(2013). Ultimate analysis of sample was performed with Elemental analyser currently available at CRDT (centre for rural development and Technology) -IIT Delhi, that determine the carbon, hydrogen, nitrogen, and oxygen percentage. Oxygen content was obtained by subtracting each element percentage from 100%. Thermal gravimetric analysis (TGA) of the sample were performed at CSIR-NIEST Jorhat, Assam. Thermal analysis used to measure the mass change of a sample being heated at constant rate of 10^{0}C/min in an inert environment. It helps to understand the nature of feedstock and how sample behave at various temperature. This will help to understand the how feedstock will behave under pyrolysis and at what temperature breakdown of various component of biomass will occur (Hopkins, 1997).

FTIR analysis of raw sample and its char was carried out with Thermo-scientific IS 50NIR at central research facility of IIT-Delhi. FTIR produces markedly superior spectra and can provide more precise information concerning the oxidation of carbons and the formation of carbon-oxygen surface groups. This technique can also allow measurements of lower concentrations of surface functional groups (Group, 2005). SEM analysis was performed at Central research facility at IIT-Delhi. Iodine number and BET both value defines the adsorption capacity of a porous material. Iodine number of biochar and activated biochar can be found with the help of ASTM D4607 –14. In this Iodine solution is titrated against standardized sodium thiosulfate with starch as an indicator before adsorption for standardization of iodine. Adsorption of iodine is performed in an acidic environment to remove any sulphur within the sample. After adsorption of iodine, filtrate is titrated against the standardize sodium thiosulfate. Brunauer–Emmett–Teller equation or BET analysis of biochar was carried out in Lab of Chemical Engineering at IIT-Delhi on BELSORP-maxII. Experiment was carried out in the presence of nitrogen at 77.36K.

2.4 Adsorption Experiment

Adsorption experiment was performed at room temperature 25±3^{0}C with enriched biogas produced within the Biogas Laboratory CRDT at IIT-Delhi. Biogas was produced using kitchen waste within IIT-Delhi campus(Isha et al., 2020). Biogas was enriched with the help of water scrubbing column (Kapoor et al., 2017). Enriched biogas was analysed with help of biogas analyser from GEOTECH "BIOGAS 5000". Enriched biogas was stored in a rubber balloon of 6m^3 which was further processed for compression with the help of Coltri compressor (Made in Italy) into a CNG cylinder. This cylinder was removed from compressor and connected to ABG cylinder that was stationed on an electronic balance. ABG cylinder was fitted with a thermocouple and a pressure gauge as shown in figure 1. Enriched biogas was introduced to the ABG cylinder in a controlled way using manually operated valve. Experiment was performed for 5th cycle for each filler. One cycle consists of charging and discharging of cylinder with enriched biogas. Residual amount of enriched biogas after 5th was noted down.



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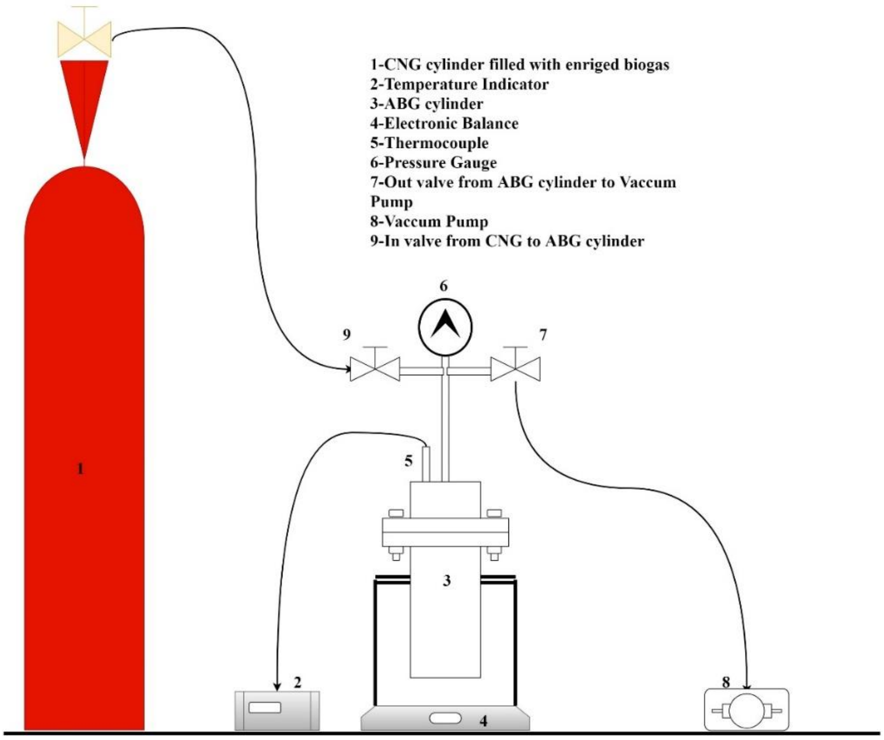

B

Figure 2. A) is showing setup for compressing enriched biogas into CNG cylinder, B) Experimental setup for adsorption of enriched biogas.

3. Result and discussion

3.1 Proximate and Ultimate Analysis

Under rudimentary test Proximate analysis plays an important role as it is comprised of moisture content, ash content, volatile matter, and fixed carbon. For biochar it is very crucial to know the element percentage. Ultimate analysis is a very quick way to determine the elements within any organic material, mainly carbon plays a huge role in an adsorption process. In proximate analysis, ash content increases for biochar in comparison to raw biomass sample as shown in Table 1. Also, the overall carbon content increases in the biochar of both sample i.e., pigeon pea and bamboo. Increase in carbon content improves the adsorption capacity.

Table 1. Proximate and ultimate analysis of pigeon pea stalk, bamboo, and their biochar with ultimate analysis of Coconut activated biochar

Sample	Proximate Analysis				Ultimate Analysis			
	Ash Content % by wt.	Volatile matter % by wt.	Fixed Carbon % by wt. *	Moisture Content % by wt.	Carbon Content % by wt.	Hydrogen Content % by wt.	Nitrogen Content % by wt.	Oxygen Content % by wt.*
Pigeon pea stalk (a.r.b)	1.063 1.099	74.709 74.548	12.630 12.799	11.596 11.552	--	--	--	--
Pigeon pea stalk (d.b)	1.112 1.128	84.162 84.368	14.725 14.502	--	38.18	1.022	0.279	60.51
Pigeon pea stalk biochar (d.b)	4.3560 4.0424	30.911 30.561	64.732 65.395	--	70.93	2.801	1.007	25.26
Bamboo (a.r.b)	1.882 1.795	69.708 69.526	14.668 14.598	14.236 14.008	--	--	--	--
Bamboo (d.b)	2.6497 2.6783	80.655 80.395	16.694 16.926	--	50.86	2.168	1.32	45.65
Bamboo biochar (d.b)	10.781 10.053	19.548 19.921	69.669 70.025	--	74.13	5.527	0.148	20.19
Coconut activated biochar (d.b)	--	--	--	--	85.59	2.195	0.6	11.61

a.r.b= as received basis, d.b = dry basis, * = subtraction method

3.2 Thermal gravimetric analysis (TGA)

This measurement provides information about physical phenomena such as desorption and chemical phenomena such as (Coats and Redfern, 1963). Differential thermogravimetric (DTG) curve obtained for pigeon pea stalk and bamboo is shown in figure 3. Region, in between 1 and 2 before 200^0 C shows the removal of moisture. After point 2 hemi cellulose and cellulose start to break down. Passing through point 3 shows faster decomposition of biomass whereas at 4 decomposition slows down and lignin start to break down until it reaches to point 5 where maximum portion of biomass converted to gas. Beyond point 5 lignin further breakdowns at very slow rate. At point 6 maximum portion of biomass decomposes and remaining portion of biomass represents its ash content(Huang et al., 2016).

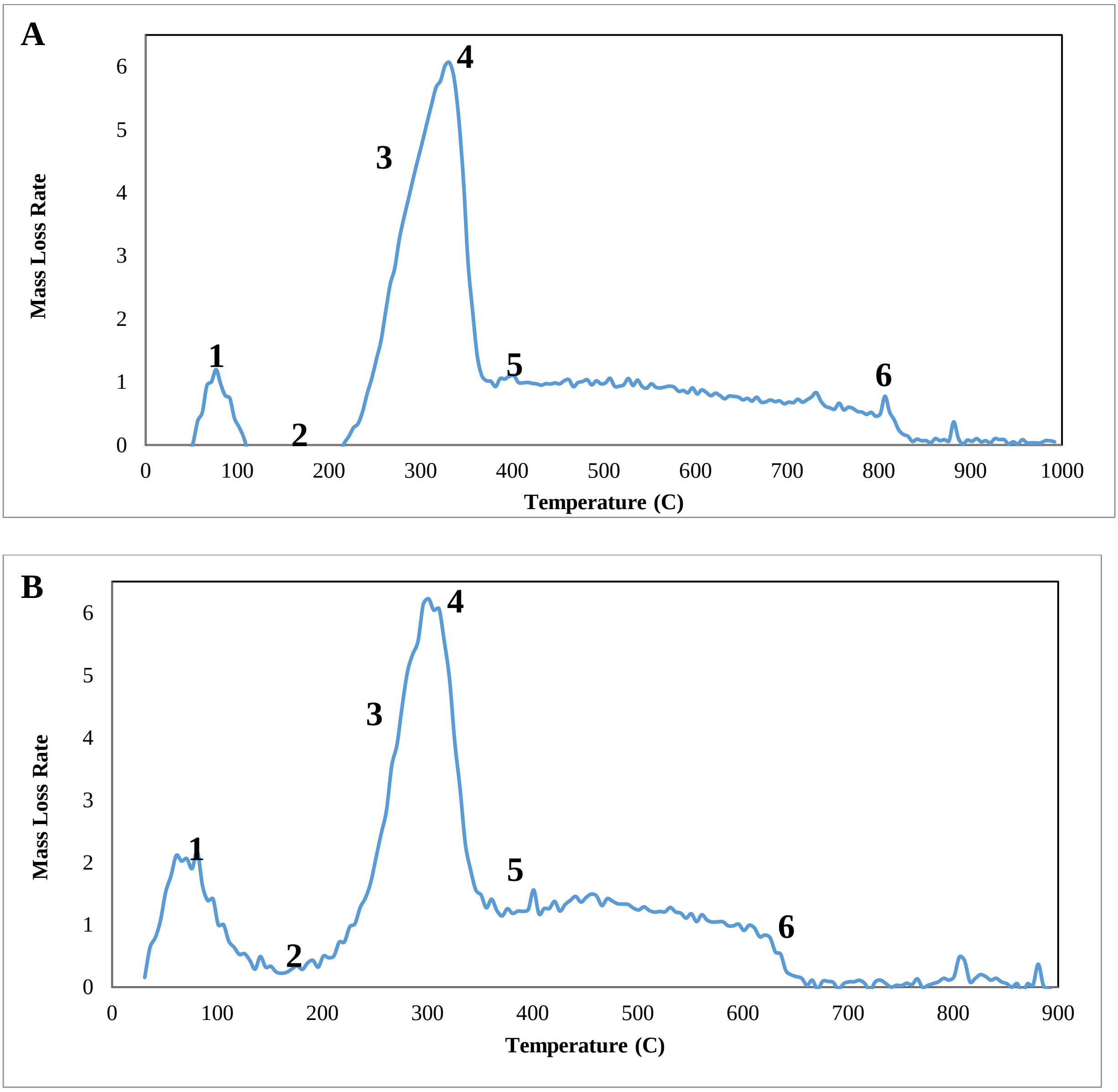

Figure 3. Differential thermogravimetric analysis of pigeon pea stalk (A) and bamboo (B)

3.3 *Fourier-transform infrared spectroscopy (FTIR)*

Graph produced between wavenumber and transmittance is shown in Figure 4. Peak at a particular wavenumber corresponds to a distinct functionality as mentioned in Table 2.

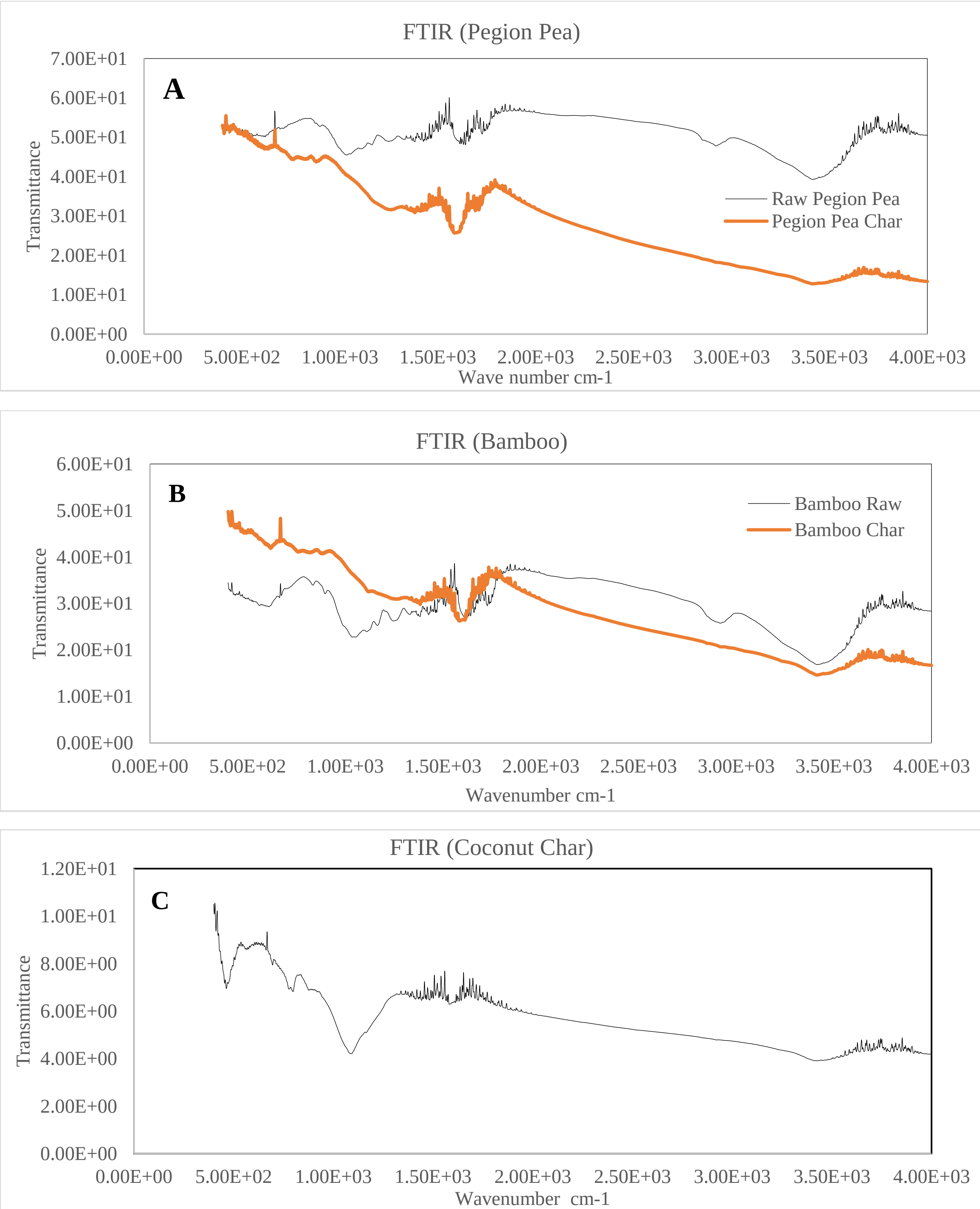

Figure 4. FTIR analysis of A) pigeon pea stalk and its biochar, B) bamboo and its biochar, C) Coconut activated biochar.

Table 2. Following table show different functional group corresponds to different wavenumber (Cantrell et al., 2012).

Wave number (cm^{-1})	Characteristic vibrations (functionality)
3500–3200	O–H stretching (water, hydrogen-bonded hydroxyl
2935; 2885	C–H stretching (aliphatic CHx; 2935-asymmetric, 2885-symmetric
1740-1700	C=O stretching (carboxyl, aldehyde, ketone, ester
1653-1645	N–C=O (amide I: carbonyl stretching vibration in peptide bond
1600-1595	CC=C, C=O, C=N (aromatic components conjugated ketones and quinones, amide, amine)
1514	C=C, N–H (secondary aromatic amines, pyridine rings)
1440	C=C stretching; –C–H2 bending (lignin carbohydrate)
1375	O–H bending (phenolic; ligneous syringyl)
1110	Symmetric C–O stretching (C–O-C in lignocelluloses)
1100–950	P–O (asymmetric and symmetric stretching of PO2 and P(OH)2 in phosphate)
1030	Symmetric C–O stretching (cellulose; hemicellulose; methoxy groups of lignin)
885	C–H bending (aromatic CH out-of-plane deformation)
781	Pyridine (pyridine ring vibration and C–H deformation)
635	Phenyl ring vibration (Kumar et al., 2020)

In all biochar sample there is reduction of OH group showing at 3500 cm^{-1}. In Fig. 4-A and 4-B peak around 2900 cm^{-1} shows the presence of aliphatic hydrocarbon. In case of biochar at 2900 cm^{-1} there is no peak showing break down of its component. Above 1500 cm^{-1} and below 1700 cm^{-1} wide stretch of aromatic hydrocarbon was found in raw biomass and biochar of both sample. In this range coconut biochar shows no peak which indicates absence of aromatic hydrocarbon. Around 600 cm^{-1} in case of pigeon pea and its char shows the presence of phenolic ring.

3.4 *Scanning Electron Microscope (SEM)*

SEM used to read the surface morphology of various samples. For Biochar this is used see the porous structure created on the surface. There is a drastic change in surface morphology on comparing raw sample to its biochar. Macroporous structure had formed in both biochar. In case of coconut biochar not much of macroporous structure can be seen as shown in figure 5.

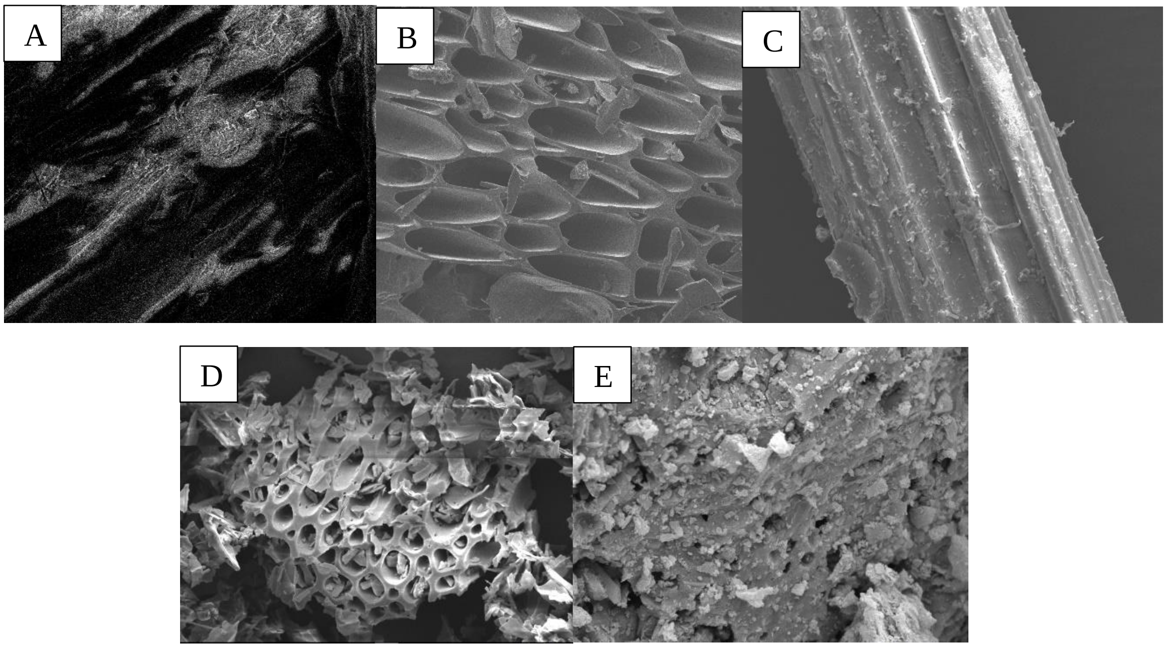

Figure 5. A) SEM of raw pigeon pea stalk, B) SEM of pigeon pea biochar, C) SEM of raw bamboo, D) SEM of bamboo biochar, E) Coconut activated biochar.

3.5 *Iodine number and Brunauer–Emmett–Teller (BET) Test*

Iodine number gives the amount of iodine adsorbed by an adsorbent per gram which gives an idea of porosity present within a porous material. Value of Iodine number for biochar is low comparative to activated biochar as mentioned in table 3. Generated graph with BET method is very help full for explaining macroporous or non-porous surface as shown in figure 6. It not only gives an idea of about surface area, but it also tells us about the adsorption characteristics(Group, 2005).

Table 3. Iodine number and Surface area of different biochar

Sample	Pigeon pea Biochar	Bamboo biochar	Coconut activated biochar
Iodine Number (mg/g)	106.4	87.14	920.04
BET surface area (m^2/g)	85.67	30.01	957
Total pore volume (cm^3/g)	0.0697	0.0272	0.5427
Mean pore diameter (nm)	3.2586	3.634	2.2662

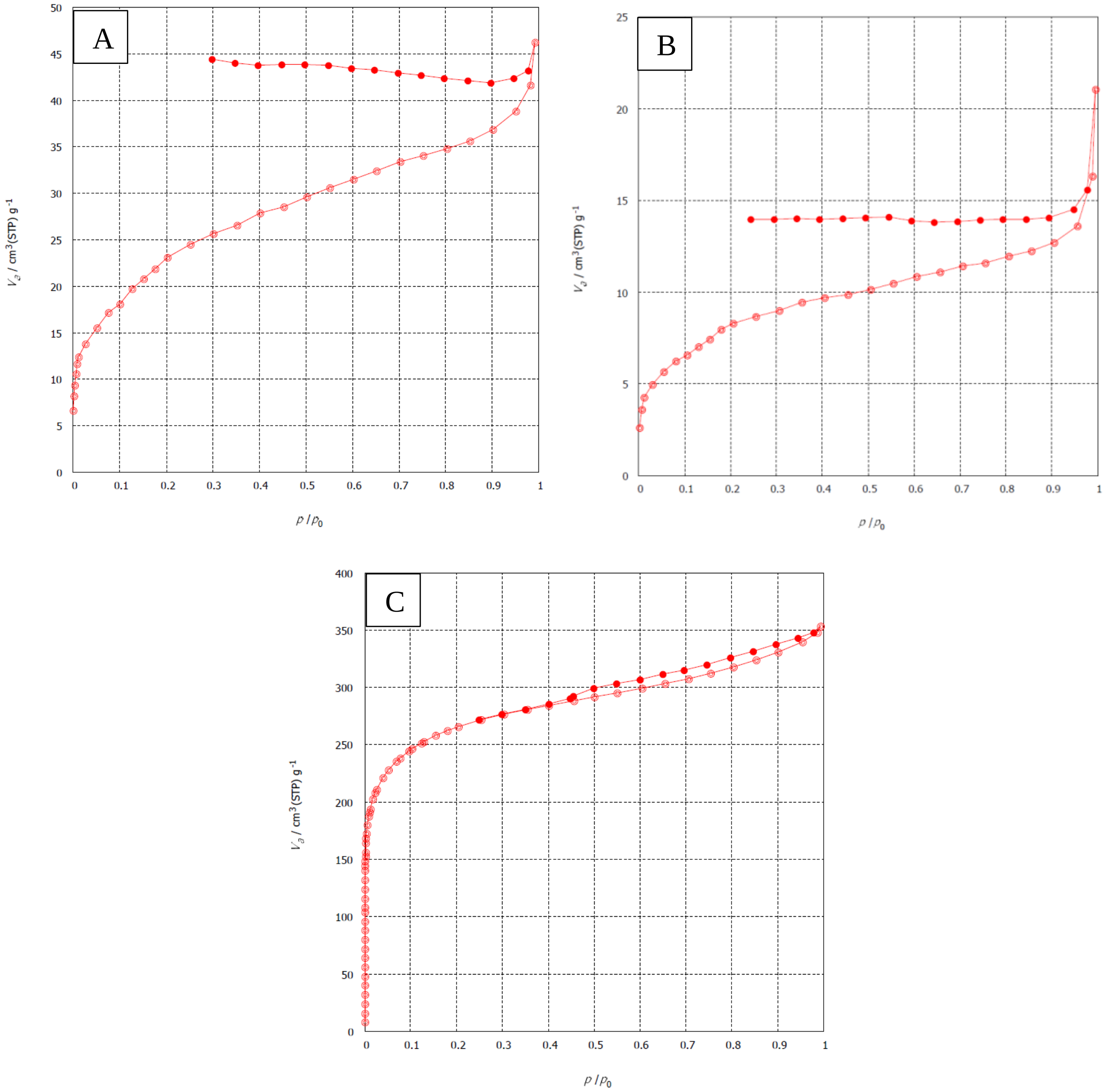

Figure 6. Graph represents adsorption isotherm for A) pigeon pea biochar, B) bamboo biochar, C) Coconut activated biochar.

3.6 Adsorption of Enriched Biogas

Pigeon pea stalk biochar was used for Adsorption of enriched biogas in ABG cylinder. A storage cylinder of volume 2.831L with a design pressure of 30 bar pressure capacity was used for experiment. A CNG cylinder was filled with enriched biogas and connected to ABG cylinder. Pigeon pea and bamboo biochar was filled in the cylinder with a tapped bulk density of 379g/L and 346g/L respectively. Whereas the coconut activated biochar has a tapped bulk density of 410g/L was of Following is specification of enriched biogas.

Table 4. Specification for Enriched Biogas

Methane % by wt.	Carbon dioxide % by wt.	Oxygen % by wt.	Hydrogen Sulphide % by wt.	Nitrogen% by wt.
88.8	4.5	1.0	0.0011	5.6

Before the experiment, vacuum pump was utilized remove the air from ABG cylinder. Removing of air was performed for half hour. Experiments on ABG cylinder was performed in both ways with and without biochar. Maximum amount of gas that was stored in ABG cylinder was 75 g at 20 bar pressure using granular coconut activated biochar as mentioned in table 4. Residual amount of gas that was present at end of 5 cycle was 0 g for granular coconut activated biochar as shown in table 5.

Table 5. Amount of enriched biogas gas stored when ABG cylinder was filled with distinct filler.

Distinct Filler	Maximum Amount enriched biogas stored at 20bar Pressure for different filler(g)
Without any Adsorbent	44
Filled with Pigeon pea stalk char	54
Filled with bamboo char	41
Filled with Coconut activated biochar	75

Table 6. Maximum Amount enriched biogas resides within cylinder after 5th cycle with distinct filler

Distinct Filler	Maximum Amount of enriched biogas resides within cylinder after 5th cycle (g)
Without any Adsorbent	0
Filled with Pigeon pea stalk char	6
Filled with bamboo char	4
Filled with Coconut activated biochar	0

Result clearly shows that the adsorption capacity of activated biochar with high surface area shows the maximum storing amount at 20 bar pressure.

4. Conclusion

This study indicates the possibility of storing more enriched biogas at low pressure with the help of a porous material. Considering the case of biochar and activated biochar, activated biochar shows enhanced storing capacity. This is due its high surface area. Currently biomethane can be stored at high pressure at 200 bar but in future, ABG can store the same amount of enriched biogas or biomethane at 20 bar pressure. On achieving this goal, this technology can be further applied to mobile and stationary application. Rural aspect of this application will be storing of biomethane that is produced with in a rural area.

5. Acknowledgments

Experiments and research paper draft were produced by Sameer Ahmad Khan. Komalkant Adlak and Ujjiban Kakati helped in BET (Brunauer Emmet Teller) analysis and thermogravimetric analysis respectively. Whole work was performed under the supervision and guidance of Dr. Ram Chandra and Prof. Virendra Kumar Vijay.

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