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Corn Stover as Substrate for Biogas Generation and Precursor for Biosilica Production via Anaerobic Digestion

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Abstract

Production of fuels and chemicals from renewable biomass is crucial to sustainability of bio-based economy. In this study, anaerobic digestion of corn stover (CS) was carried out to produce biogas under mesophilic conditions. The study also investigated the potential of corn stover digestate ash as a potential source for biosilica production. A cumulative volume of 930 mL of biogas was produced with methane content of 85.87%. Higher and lower calorific values of biogas were calculated to be 36.30 MJ/m^3 and 32.70 MJ/m^3, respectively. Calcination of raw CS (RCS) and the digestate (CSD) was carried out at 600 °C for 3 hours. The samples generated, raw corn stover ash (RCSA) and corn stover digestate ash (CSDA) were characterized using X-ray fluorescence (XRF), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), and X-ray diffractometer (XRD). The XRF results revealed that CSDA biosilica content was 60.49%, which was 34.84% higher than RCSA. There was reduction in most of the metallic impurities in CSDA compared to RCSA. Potassium oxide was drastically reduced from 12.34% to 1.60%, while Al_2O_3 was reduced from 7.17% to 6.95%. SEM images showed the changes in the surface morphology of RCSA and CSDA, while FTIR spectra identified the changes in the key functional groups present in the samples. The study showed that CS and its digestate could serve as profitable renewable feedstocks for bioenergy production and bio-based chemicals like silica.

Keywords: Anaerobic Digestion; Biogas; Biosilica; Corn Stover; Digestate; Calorific Value

Introduction

Global transition to clean energy and production of value-added chemicals and materials from renewable sources based on the concept of biorefinery comes with its challenges and opportunities (Philp 2018). One of such challenges is in the area of anaerobic digestion (AD) where enormous quantities of digestates are generated. AD is an environmentally benign technology that converts organic biomass to biogas (methane and carbon dioxide) with the aid of microorganisms in the absence of oxygen (González et al. 2018). The digestates which are the by-products of AD are made up of liquid and solid fractions that are mostly used as biofertilizers (Koszel and Lorencowicz 2015). However, with AD technology gaining prominence and acceptance in many quarters as alternative source of energy, large quantities of digestates are equally produced that need to be managed appropriately. Although some research efforts aimed at increasing and providing alternative use for digestates have been carried out (Achinas et al. 2017, Czekala 2017, Kaur et al. 2020) yet a lot still has to be done as a forward-thinking approach to mitigate the problems from unused digestates. For instance, biofuels like briquettes and pellets have been produced from solid fractions of digestates (Czekala 2017, Czekała et al. 2018). There is need for sustainable techniques to produce more valued-added products from these digestates in order to increase their usefulness, prevent their being sources of environmental concern and invariably enhance competitiveness of bio-based industries. Otherwise, in a bid to solve one problem we may be unwittingly creating another with far reaching effects on humans and the environment.

Mirmohamadsadeghi and Karimi (2018) produced amorphous silica from the ash of digestate from rice straw in a more environmentally friendly manner than the capital intensive conventional method of producing silica. Numerous temperature regimes have been used to prepare biosilica with the conclusion that combustion temperature and time played crucial roles in producing biosilica of high quality (Terzioğlu et al. 2019). Silica finds applications in various industries such as food, paint, and cosmetics industries (Permatasari et al. 2016).

Corn stover (CS) is an agricultural waste remaining in the field after harvesting corn (Paul et al. 2019). Corn is a major staple crop in Nigeria that enjoys two planting seasons in a year, thus huge amounts of it are produced annually. Nigeria is the tenth largest producer of corn in the world and the highest in Africa (IITA 2020). Therefore, corn stover is one of the major agricultural wastes produced in Nigeria and it is highly underutilized for any profitable uses. Production of second generation biofuels like biogas and other value added products like silica from CS would help convert a liability to valuable asset. However, it is worth mentioning that corn stover can be used for erosion control and it is also a source of soil nutrients like phosphorus and potassium (Bashagaluke et al. 2018, Wang et al. 2007). The objectives of the study therefore were to produce biogas from CS under mesophilic conditions, calculate its calorific value, and evaluate the biosilica potential of the ash of the digestate using XRF, FTIR, SEM, XRD in comparison with the ash of raw CS.

Materials and Methods

Corn stover was collected in June 2018 from a local farm in Irrua in Esan Central Local Government Area, Edo State, Nigeria. The corn stover was sun-dried for three weeks and pulverized to reduce the particle size. Afterwards, the sample was passed through a 600 microns mesh sieve. The sample was stored in an air-tight container prior to analysis and anaerobic digestion.

Anaerobic digestion

Batch laboratory AD of raw corn stover (RCS) was carried out at particle size of 600 microns. A sample of 100 grams was mixed with 400 mL of water (solid-to-liquid ratio of 1:4) and charged into a 1-L glass bioreactor for a retention time of twenty-one days at an ambient temperature of 26 ± 1 °C. Cumulative biogas produced was measured by downward displacement method with saturated salt solution every 24 hours (Adamu 2014). Initial and final pH values were measured using a digital pH meter by HANNA Instruments. Methane content was determined using chemical absorption method as described by Lasocki et al. (2015). Volatile solid reduction (VSR) was calculated by the method described by Puyuelo et al. (2011). Higher calorific value (HCV) and lower calorific value (LCV) of biogas from the digester were determined according to the following formula:

$$HCV_{biogas} = 0{:}3989 \text{ x } MC + 0{:}0213 \quad (1)$$

LCV_{biogas} = 0:3593 x MC + 0:0192 (2)

Characterization of raw corn stover and digestate corn stover

Moisture content, total solid, ash content, carbon, nitrogen, lignin, cellulose and hemicellulose of raw CS and the solid fraction of its digestate were determined using standard methods (ASTM 1972, Horwitz 2000).

Preparation of ashes of raw corn stover and digestate

The solid fraction of corn stover digestate was separated from the liquor and sun-dried for three days. The dried digested CS was calcined at 600 °C for 3 hours along with the raw CS. The resulting raw corn stover ash (RCSA) and corn stover digestate ash (CSDA) were kept in air-tight containers for analyses.

Characterization of raw corn stover ash and corn stover digestate ash

The chemical compositions of raw corn stover ash (RCSA) and corn stover digestate ash (CSDA) were determined using an energy dispersive X-ray fluorescence (XRF; Xsupreme 8000 Model, Oxford Instrument). The X-ray diffraction (XRD) patterns of RCSA and DCSA samples were recorded using XPert PRO model, Netherlands. The samples were scanned in the 2θ range of 5° to 90°. The functional groups were determined using FTIR spectroscopy, while surface morphology was carried out using SEM.

Results and Discussion

Anaerobic digestion of corn stover

Table 1 shows physicochemical properties of raw CS and its digestate. There was increase in ash content after anaerobic digestion which is an indication of increased mineral content in the digestate. This shows that the digestate could be used as a biofertilizer (Dahunsi et al. 2019). A high VS/TS ratio of 0.84 was a confirmation that the substrate had appreciable quantity of digestible organic materials. The VS/TS was similar to 0.87 reported for banana peel waste by Achinas et al. (2019). There was increase in lignin and hemicellulose contents after anaerobic digestion; this observation has been reported in literature (Waliszewska et al. 2019). The cellulose content in the raw sample was relatively high, which is beneficial for anaerobic digestion. The reduction in the cellulose content after digestion revealed that the microorganisms were capable of degrading the cellulose for bioenergy generation. Initial pH value was 6.50, while the final pH was 3.10; this obvious reduction in pH has been attributed to the increase in volatile fatty acid production during AD process (Xu et al. 2013).

Table 1: Physicochemical properties of raw corn stover and corn stover digestate

Parameters (%)	Raw corn stover	Corn stover digestate
Moisture content	3.00	7.00
Ash content	15.27	24.45
Total solids	97.00	93.00
Volatile solids	81.73	68.55
*VS/TS	0.84	0.74
Lignin	12.30	15.50
Cellulose	53.30	48.74
Hemicellulose	34.40	35.76

*VS/TS has no unit.

Daily biogas production from raw CS is shown in Figure 1. Biogas production commenced on day 1 which revealed that the initial lag phase was short, which is an indication of rapid acclimatization of the microorganisms to the substrates. However, there was a decline in production after some days followed by days of little (represented by short peaks) or no production till the end of the experiment. Kafle and Kim (2013) have suggested that the diauxic phase experienced in the biogas production could be attributed in part to the presence of easily digestible and non-easily digestible components in the substrate. Figure 2 shows cumulative biogas production of the sample which was 930 mL at the expiration of the digestion process. Volatile solid reduction (VSR) was calculated to be 50.97%, which was similar to 50.49% reported for anaerobically digested cow manure in a hydraulic mixed Chinese dome digester by Jegede et al. (2019). Cumulative methane content from RCS was calculated to be 85.87% using chemical absorption method. This value was higher than 72.30% reported by Pertiwiningrum et al. (2018). Equations 1 and 2 were used to calculate the HCV_{biogas} and LCV_{biogas} for methane in this study, which were 34.28 MJ/m^3 and 30.87 MJ/m^3. The values for HCV_{biogas} and LCV_{biogas} were comparable to 36.30 MJ/m^3 and 32.70 MJ/m^3 reported for anaerobic codigestion of buffalo grass and dung by Chuanchai and Ramaraj(2018). On the other hand, the values were higher than 23.8 MJ/m^3 and 21.50 MJ/m^3 reported for municipal solid wastes by Triana-Jiménez et al. (2019). The HCV_{biogas} and $LCV_{biogas\ for}$ CS seem satisfactory when compared to that of pure methane which is 39.82 MJ/m^3 and 35.87 MJ/m^3, respectively (Li et al. 2017).

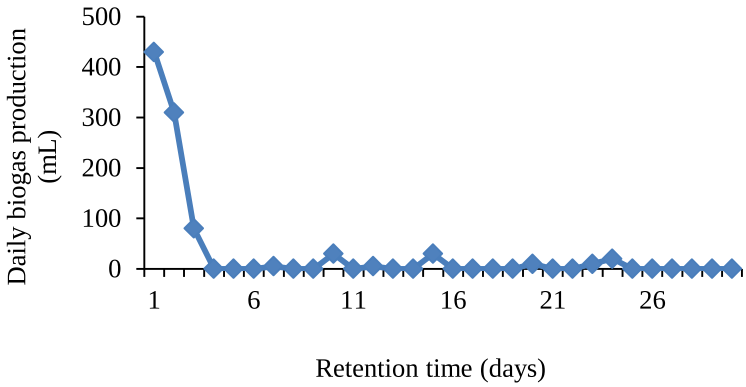

Figure 1: Daily biogas production of corn stover.

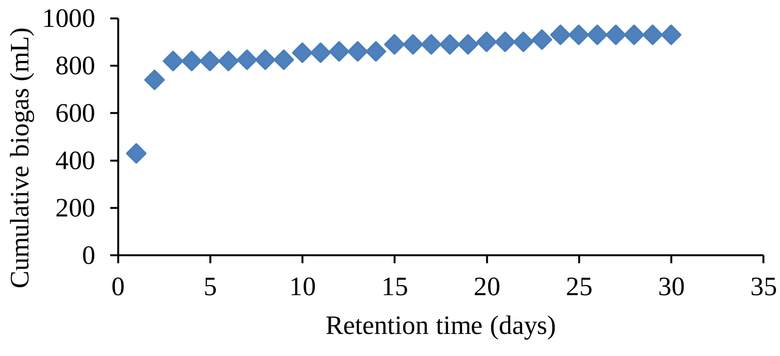

Figure 2: cumulative biogas production from corn stover.

Chemical analysis of RCSA and CSDA

Chemical composition results for RCSA and CSDA are shown in Table 2. The SiO_2 content of CSDA was 60.49% which was 34.84% higher than that of RCSA. The value obtained for SiO_2 in CSDA was higher than the 39.95% and 43.22% reported for maize stalk and wheat hull by Terzioğlu et al. (2013),but lower than the 71.50% recorded for raw bagasse ash by Tadesse et al. (2019).

There was a significant reduction in K_2O impurity after anaerobic digestion from 12.34% to 1.60% but not Na_2O which increased significantly after AD. The decrease in K_2O after AD is in agreement with the findings of Mirmohamadsadeghi and Karimi (2018) on the production of amorphous nanosilica from rice stalk digestate. A decrease in the contents of Al_2O_3 and SO_3 was also observed. This is advantageous as their presence in high amount has been implicated for reduced usefulness of biosilica (Adebisi et al. 2017). The observed reduction in metallic oxides as a result of AD is indicative of higher purity and a welcome development from economic standpoint since removal of impurities in biosilica is normally carried out by a relatively expensive acid leaching method (Khalifa et al. 2012, Suryanto et al. 2018).

Table 2: Chemical analysis of RCSA and CSDA by X-ray fluorescence

Sample	SiO_2	K_2O	CaO	MgO	Na_2O	Al_2O_3	P_2O_5	Fe_2O_3	Mn_2O_3	Cl	SO_3	TiO_2
RCSA	44.86	12.34	6.20	5.81	0.95	7.17	8.44	8.65	0.17	0.97	3.55	0.73
CSDA	60.49	1.60	4.18	2.24	4.34	6.95	2.98	10.02	0.13	2.80	3.08	1.03

Physical appearances of RCSA and CSDA are shown in Figure 3. The ash of RCSA was greyish in colour, while that of CSDA was brownish. The variation in colour could be as a result of the transition metal oxides present in the samples (Terzioğlu et al. 2019)

Figure 3: Physical appearances of a) raw corn stover ash (RCSA) b) corn stover digestate ash (CSDA).

Functional groups analysis of the studied corn stover samples

Figure 4 shows the infrared spectra of the corn stover digestate (CSD), corn stover digestate ash (CSDA), raw corn stover (RCS) and raw corn stover ash (RCSA) with different levels of intensity. The Si-OH (silanol) peak at about 3130-3712 cm^{-1}(Mirmohamadsadeghi and Karimi 2018) is evident in all the samples. The appearance of the band at 2844–2988 cm^{-1} in the spectrum of the CSD and RCS is attributed to the stretching of CH_2 bonds of polysaccharides (Mirmohamadsadeghi and Karimi 2018). The observed band was absent in the CSDA and RCSA samples after subjecting them to calcination. This could be due to the degradation of the polysaccharides molecules brought about by calcination at 600 °C for 3 hours. This is aclear indication that calcination carried out on the samples at this temperature had brought about some significant changes in the samples. The calcination temperature of 600 °C used in this study falls within the range reported in literature as appropriate for the production of biosilica (Memon et al. 2020, Wang et al. 2019).

Sharp bands were visible in the spectra at 1628 cm^{-1} for lignin moieties (Chen et al. 2012, Pandey 1999) in all the samples (CSD, CSDA, RCS and RCSA). The peak at 1386 cm^{-1} in the spectrum of the CSD, CSDA and RCS samples are suggestive of the presence of weak C-O stretching in cellulose (Wetzel et al. 1998, Xu et al. 2013, Yu et al. 2007). However, this peak was not observed in the spectrum of RCSA, instead, there was an appearance of a broad peak at 1368–1530 cm^{-1}. The peak at 796 cm^{-1} can be ascribed to the symmetric vibration of Si–O (Mirmohamadsadeghi and Karimi 2018) in CSD and CSDA. The absence of this peak in the RCS and RCSA samples maybe because they were not subjected to anaerobic digestion. The peak of aliphatic C-O-C groups at 1028–1092 cm^{-1} can be attributed to the presence of hemicellulose and cellulose (Rafiq et al. 2016) in all the samples. This is indicative of incomplete charring of the RCSA and CSDA, at this temperature (Chen et al. 2008, Rafiq et al. 2016). The peak at 466 cm^{-1} observed in all the studied samples has been attributed to the presence of silica (O-Si-O) (Ifijen et al. 2020, Mirmohamadsadeghi and Karimi 2018).

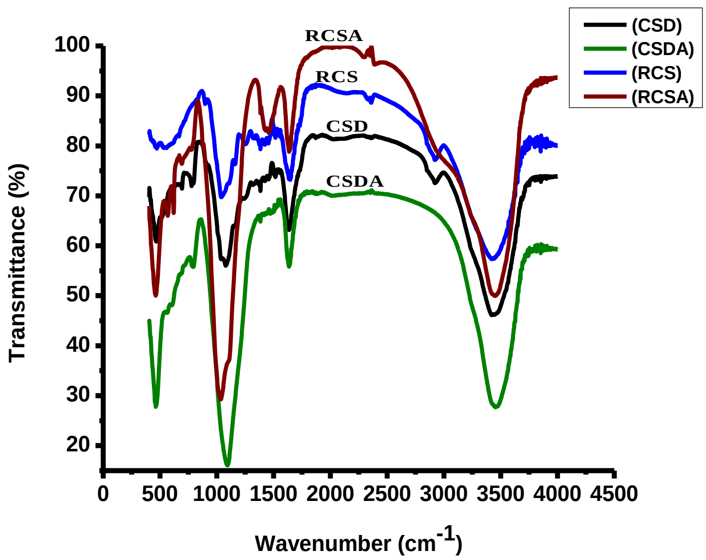

Figure 4: FTIR spectra of raw corn stover (RCS), raw corn stover ash (RCSA), corn stover digestate (CSD) and corn stover digestate ash (CSDA).

Analysis of the crystalline and amorphous nature of CSDA and RCSA samples

Figure 5 shows the XRD pattern of the samples of raw corn stover ash (RCSA) and corn stover digestate ash (CSDA). XRD results revealed the emergence of multiple peaks at several regions of the raw corn stover ash. Narrow peaks were located at 2θ values of 7.9°, 9.5°, 11.3°, 12.5°, 17.1, 21°, 23.0°, 26.5° and 30.1°. Broad peaks which were not intense were also observed in other regions of the RCSA. The observed results are indications that the analyzed RCSA had more crystalline regions than amorphous regions. The observed peaks may also be due to the presence of the elemental oxides impurities detected by the XRF (Table 2) and cellulose lattice. On digestion of the studied material, most of the aforementioned peaks that appeared before anaerobic digestion disappeared completely leaving behind two narrow intense peaks at 2θ values 21.0° and 23.5° for the corn stover digestate ash (CSDA). The observed two narrow, sharp peaks at 2θ values around 21.5° and 23.8° could be attributed to the partial crystalline regions of the cellulose content and silica regions, respectively (Fernandes et al. 2017, Singh et al. 2015).

The peaks have been attributed to the presence of cristobalite, a crystalline form of silica (Fernandes et al. 2017). The disappearance of the numerous peaks in CSDA could be indicative of reduction in its crystalline nature. The peak that appeared at the angle of 23.5° can be attributed to the presence of partial crystalline silica.

However, the silica synthesized via other sources at 2θ = 23.5 have been shown by several studies to be completely amorphous in nature (Fernandes et al. 2017, Kalapathy et al. 2000, Kamath and Proctor 1998).

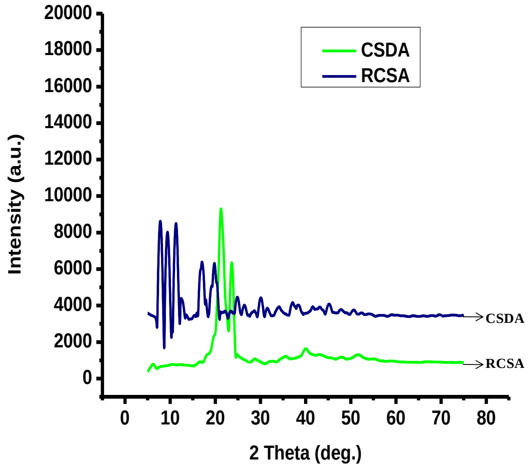

Figure 5: X-ray powder diffraction (XRD) spectra of ashes of raw and digested corn stover

Morphology of the RCSA and CSDA samples

Figure 6 shows the SEM mages of samples RCSA and CSDA. Sample RCSA had a coarse, clustered surface, while sample CSDA had lesser clustered surface (loosened) and more porous than RCSA. Activities of the anaerobic microorganisms could have been responsible for the observed changes.

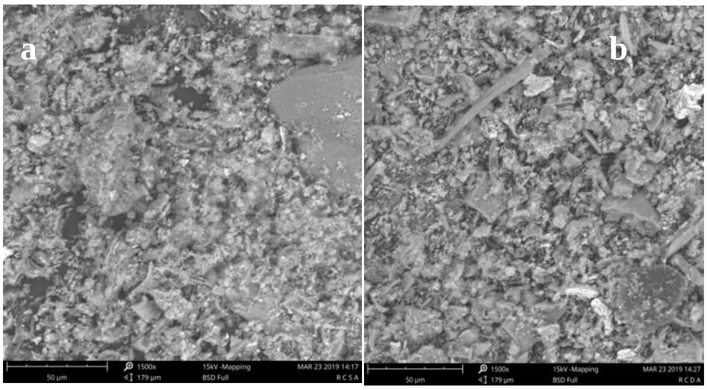

Figure 6: The SEM images of a) raw corn stover ash and b) corn stover digestate ash.

Conclusion

This study revealed that CS is a valuable substrate for biogas production with high methane content of 85.87%. The high calorific value of 36.30 MJ/m^3 obtained in this work further proved the quality of biogas from CS. The SEM images revealed that CSDA was more porous and less coarse than RCSA, while the XRD results showed that CSDA had less crystalline regions. CSDA showed a remarkable improvement in biosilica content in comparison to RCSA as revealed by the XRF. The results further demonstrated that CSDA had higher puritythan RCSA based on reduction in metallic oxides impurities which was an indication that AD was effective in reducing some of the metallic impurities. Therefore, AD could serve as an alternative to relatively expensive chemical treatment usually employed to improve the quality of biosilica, while at the same time increasing product yields.

Conflicts of interest/Competing interests:
The authors declare no conflict of interest.

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