ENHANCEMENT OF BIO-METHANE PRODUCTION BY LIGNOCELLULOSE SUBSTRATES

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ABSTRACT: In this study, water hyacinth, sweet sorghum bagasse and amaranth stems were used in a pig manure matrix to produce biogas with a high methane content. The anaerobic digestion was monitored over a period of 40 days, after which the biogas production significantly decreased. Samples were taken of the gas and the leachate every 5 days to monitor the production of gas and to evaluate the formation of volatile fatty acids in the leachate. The pH of the leachate was monitored using a pH meter and the cell growth in the leachate was monitored using ultraviolet spectrometry. The biogas composition was determined using gas chromatography and the volatile fatty acids in the leachate was quantified using HPLC. It was found that the addition of lignocellulose to a pig manure matrix resulted in a significant increase in the methane content and a decrease in the carbon dioxide content of the biogas. The leachate contained high amounts of volatile fatty acids such as acetic acid, lactic acid, succinic acids and butyric acid. The research showed that co-digestion in an anaerobic digester can be used to manipulate the composition of both the produced biogas and the leachate obtained after digestion.
Keywords: anaerobic, co-digestion, amaranth, sorghum, biogas, water hyacinth

1 INTRODUCTION

Presently, fossil fuels are being depleted at a rapid rate while consumption is increasing and this poses a risk to energy security. Another significant global challenge in terms of energy security resource supply is the uncertainty around the conventional gas and oil reserves that are concentrated in political unstable regions [1].

Biofuels such as biogas, bioethanol and biodiesel have received a considerable amount of attention as alternatives to fossil fuels and are perceived to provide energy security, in terms of renewability and biodegradability [2, 3, 4]. Biogas is primarily a mixture of different gases such as methane (CH_4) (50 – 60%), carbon dioxide (CO_2) (38-48%) and trace gases (2%) such as hydrogen (H_2) and hydrogen sulfide (H_2S) [5, 6].

Methane is preferred, because it is a highly combustible gas that can be used in a number of daily activities including cooking, lighting and water heating.

When methane is successfully purified from carbon dioxide, hydrogen and hydrogen sulfide, it can also be used to run biogas-fuelled generators to produce electricity [6]. Biogas productivity from a chosen feedstock is limited by the solid density and biodegradability of the material [7]. Feedstock with a low solids content thus require co-digestion with crop residues to increase biogas volume production [8]. The value of the biogas produced is to a large extent dependent on the methane content. Upgrading of biogas through CO_2 removal [9, 10] and production from lignocellulose feedstock have been reported. Biogas production from lignocellulose feedstock is limited by the biodegradability of the material [11].

In this study, the production of biogas with a high methane content from a combination of pig manure (high biodegradability) and different lignocellulose feedstock (low biodegradability) was investigated. The biogas productivity and composition at different feed ratios were monitored over a period of 43 days.

2 MATERIALS AND METHODS

2.1 Feedstock

Amaranth stem was obtained from Agricol Research Company in Potchefstroom, North West Province, South Africa (26°43'43.16"S - 27°04'47.71"E). It was dried to a moisture content of 100 $g.kg^{-1}$ amaranth and milled by hammer mill to reduce the particle size to -1.5 mm. The milled bagasse was packaged in air-tight bags and then stored at room temperature until used.

Sweet sorghum bagasse was obtained from sweet sorghum harvested at six months by the Agricol Research Company in Potchefstroom, North West Province, South Africa (26°43'43.16"S - 27°04'47.71"E). The bagasse was obtained after the juice had been pressed from the plants by roller press. The bagasse was initially dried to a moisture content of 100 $g.kg^{-1}$and milled by hammer mill to a particle size of -1.5 mm. The milled bagasse was packaged in air-tight bags and then stored at room temperature until used.

Water hyacinth was harvested from the Vaal River near Parys (26°54′S 27°27′E) in the northwest region of the Free State province, South Africa. It was initially dried to a moisture content of 100 $g.kg^{-1}$ and milled with a hammer mill. The milled bagasse was packaged in air-tight bags and then stored at room temperature unit used.

Pig manure was collected from Taaibosch Piggery, Johannesburg, South Africa (S 26°30'30.2" E 27°20'56.8) and used as collected without any drying or pretreatment to avoid degradation. The compositional analysis of the feedstock used in this study is given in Table I.

Table I: Compositional analysis of lignocellulose substrates and pig manure used in this study (A = amaranth, SSB = sweet sorghum bagasse, WH = water hyacinth, PM = pig manure)

	A	SSB	WH	PM
Dry matter	93.81	93.38	89.3	18.83
Moisture	6.19	6.62	10.7	81.17
Volatile solids	75.20	69.95	65.75	76.05
Protein	9.41	9.35	1.89	n/a
Fat extract	1.05	1.13	0.21	n/a
Ash	16.38	13.35	23.12	12.46
C-content	30.63	34.81	24.87	2.55
H-content	4.00	4.62	3.09	0.35
N-content	1.11	0.89	0.76	0.15
S and O content	64.26	59.68	71.28	96.96

2.2 Experimental method

Erlenmeyer flasks (5L) were used as bioreactors. Butyl rubber stoppers with dimensions: Top 48mm OD, Bottom 41mm OD, were used to seal the bioreactor.

Standard glass thermometers with OD 6 mm were used to detect temperature fluctuations. 5 mm OD silicon tubing was used as an outlet nozzle for the bioreactor and gas sampling bags. A pressure gauge was used to monitor the pressure build up in the bioreactor. Restek Tedlar 1L gas sampling bags were used to collect gas samples for gas chromatography analysis. All connections with the silicone tubing was clamped with cable ties. The total feed volume was 3.1 L and head space was 1.9 L. The experimental setup used in this study is shown in Figure 1.

Figure 1: Bio-digesters used in this study

In this study two bio-digesters were run concurrently with exactly the same feed. One digester was used to monitor biogas production with pressure gauge and thermometer. The other bio-digester with a sampling valve and thermometer was used to monitor the progress of anaerobic digestion. The biogas produced caused pressure build-up in the head space of the bio-digester, which is recorded by the pressure gauge. The gas produced is calculated by pressure, volume of head space as moles of the gas produced. The temperature during the course of the experiment was monitored by the thermometer during the digestion. The experimental procedure followed is given in Figure 2.

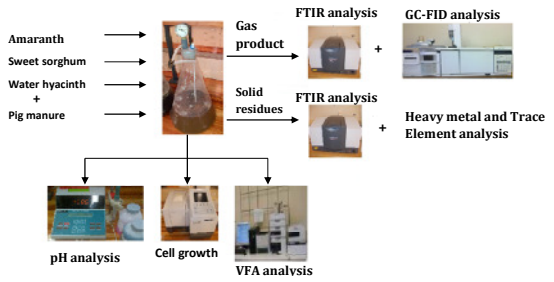

Figure 2: Experimental procedure followed during anaerobic digestion

The milled feedstock (Amaranth, sweet sorghum, water hyacinth) and pig manure were fed to the bio-digester and the reactors were then purged with nitrogen gas to ensure an inert atmosphere and sealed air tight by a rubber stopper. Biogas was collected in gas bags after every 5 days to avoid high pressure build up. The collected gas was analysed by gas chromatography (Agilent 6890A, GS-GASPRO column (60m x 0.32 mm) and fitted with a flame ionisation (FID) detector in series with a thermal conductivity detector (TCD) [3, 12]. and Fourier Transform infrared spectroscopy FTIR. Samples of the feed were taken from the bio-digester and analysed for pH, cell growth and volatile fatty acids by pH meter, Ultraviolet spectroscopy (UV) and High performance liquid chromatography (HPLC, fitted with an Aminex column and a refractive index detector) [12, 13, 14]. The composition of feed mixtures used is given in Table II.

Table II: Composition ($g.kg^{-1}$) of different feed mixtures

	P	PA	PS	PW	PAS	PAWS
PM	100	100	100	100	100	100
A	0	50	0	0	25	17
SSB	0	0	50	0	25	17
WH	0	0	0	50	0	17
C	2.6	17.8	20	15	18.9	17.9

P = Only pig manure, PA = amaranth in pig manure, PS = sweet sorghum bagasse in pig manure, PW = water hyacinth in pig manure, PAS = amaranth and sweet sorghum bagasse in pig manure, PAWS, amaranth, sweet sorghum bagasse and water hyacinth in pig manure, C= carbon content

3 RESULTS AND DISCUSSION

3.1 pH profile of the feed mixtures

The pH was monitored during the anaerobic digestion of the different feed mixtures. The pH profile for each feed mixture is given in Figure 3.

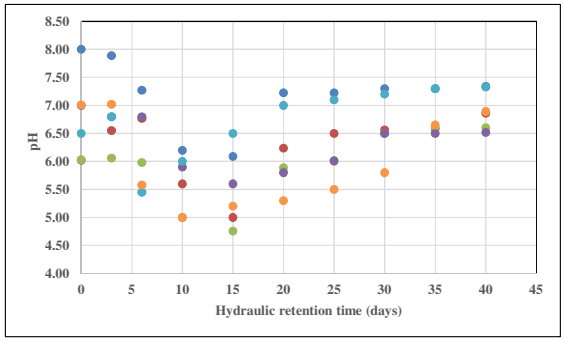

Figure 3: pH profile of liquid during digestion of the different feed mixtures (-P, - PA, - PS, - PW, - PAS, - PAWS)

The initial pH of all the experiments ranged from pH 6 to pH 8 and the final pH of all the experiments was levelled between pH 6.4 and pH 7.3. There is a pH drop between day 3 and day 20 up to acid levels of pH 4.8.

The pH of mixtures PA and PS dropped two units lower than the pH of other feedstock combination. Sweet sorghum bagasse and amaranth stem were rich in protein and fats that are converted to amino acids and fatty acids during anaerobic digestion. Amino acids and fatty acids both lower the pH. Fatty acids are further converted to hydrogen and ammonia, while amino acids are converted to carbonic acids, which have a large effect in pH drop.

During the period between day 3 and approximately day 17, the hydrolysis and acidogenesis steps resulted in the accumulation of amino and fatty acids in the digestate, causing the drop in pH. The change in pH indicates the change in the microbial community in the digestate as a result of different anaerobic digestion stages. The variation of pH from day 0 to day 2.5

indicates the hydrolysis stage of anaerobic digestion, pH change from day 2.5 to day 10 shows acidogenesis, day 10 to day 20 is acetogenesis and day 20 to day 39 is methanogenesis. There was an evident pH variation among different feedstock ratios throughout the different anaerobic digestion stages

3.2 Cell growth

The cell growth of the consortium of microorganisms in different fermentation media was monitored by analysing the cell density by UV spectroscopy. Identification of organisms present in the pig manure matrix showed the presence of *Methanocelleus sp.*, *Methanosarcina sp.*, *Methanoplanus sp.* and *Methanocorpusculum sp.* Growth curves for the consortium of microorganism for each feed mixtures is shown in Figure 4.

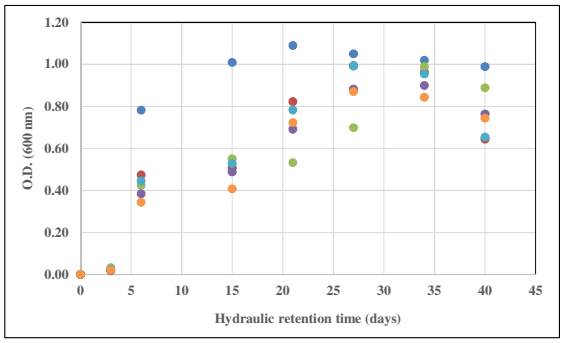

Figure 4: Growth curves for microorganism consortium in different feed mixtures (-P, - PA, - PS, - PW, - PAS, - PAWS)

The cell growth curve shows four different growth stages. The first stage was observed from day 0 to day 3 in all experiments, the second stage was observed in day 3 to day 6. The third and fourth stage differs for the different feedstock in term of days and optical density. The pure pig manure did not show any signs of the third and fourth stages. For the digestion of the mixture containing only amaranth in pig manure stage three was observed in day 6 to day 15 and the fourth stage was in day 15 to day 33. For the feed containing only sweet sorghum bagasse in pig manure, stage three was observed at day 6 to day 21 and the fourth stage in day 21 to day 33. The digestion of mixtures PAS and PAWS showed growth curves similar to that of PA in terms of stage 3 and 4. The different stages in cell density are also associated with anaerobic digestion stages. The two distinct growth stages when lignocellulose material is added to the digestion suggests the presence of additional microorganisms present only in the plant material, because the pig manure shows only one growth stage.

3.3 Biogas production

The cumulative biogas production profile from the digestion of each of the feed mixtures is given in Figure 5.

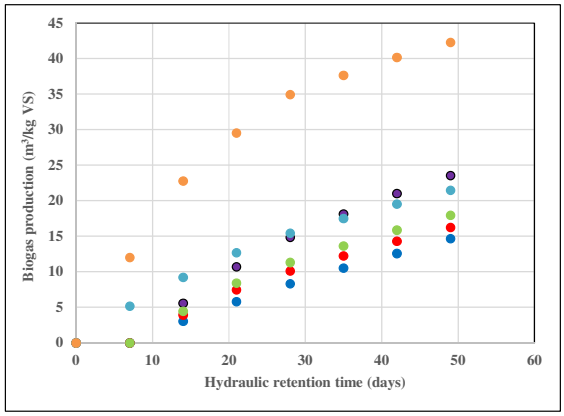

Figure 5: Cumulative biogas production from different feed mixtures (-P, - PA, - PS, - PW, - PAS, - PAWS)

The amount of biogas produced was directly influenced by the volatile solid concentration in the feed. In co-digestion of more than one feedstock the volatile solids are increased and that result in the production of high amount of biogas. All mixtures resulted in an increase in total biogas production compared to the amount of biogas obtained from the digestion of only pig manure. The mixture containing all three lignocellulose substrates in pig manure produced almost 3 times more biogas (42.3 m^3/kg VS) than the pig manure alone (14.7 m^3/kg VS). The addition of only one substrate did not significantly increase the biogas production, even though the carbon content was approximately the same as that of the mixture containing all 3 substrates. All the mixtures containing either just pig manure or one substrate in pig manure started to produce biogas only after day 14, while the mixtures containing amaranth and sweet sorghum bagasse as well as the mixture containing all 3 substrates started producing biogas from day 1.

The production of methane over the digestion period for each of the mixtures per amount of volatile solids present in the feed mixture is shown in Figure 6.

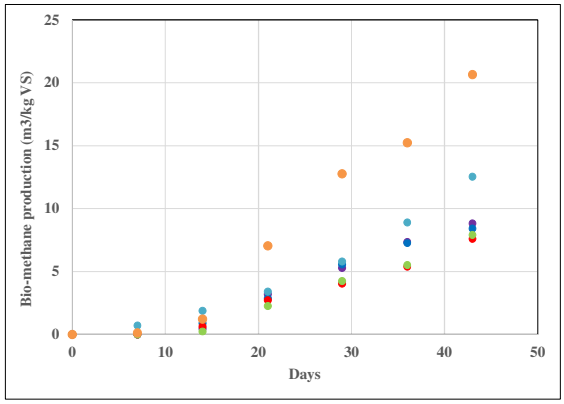

Figure 6: Cumulative bio-methane production from the different feed mixtures (-P, - PA, - PS, - PW, - PAS, - PAWS)

Methane production started on day 14 for all of the feed mixtures. The mixture containing all 3 substrates also produced the highest amount of methane per kg of volatile solids. The methane fraction in the gas is the lowest for the PW mixture (42%) and the highest for the

pure pig manure mixture (67%). The addition of lignocellulose substrates thus increased the amount of gas produced significantly, but not the methane fraction in the gas. If the gas is to be used for electricity generation, it is thus advantages to add lignocellulose to the digestate, but if the gas is to be purified to increase its value in terms of methane content, than the cost of purification will need to be balanced against the lower total gas and methane production.

3.4 Liquid residue analysis

The liquid residue after completion of the digestion was analyzed for volatile fatty acids. The amount of each acid present is listed in Table III.

Table III: Concentration ($g.L^{-1}$) of volatile fatty acids in liquid residue obtained from the digestion of the different feed mixtures

	Citric acid	Succinic acid	Lactic acid	Acetic acid	Butyric acid
PM	0	167	211	466	908
PA	72	59	106	973	948
PS	0.0	172	356	780	839
PW	95	143	86	466	608
PAS	21	467	553	871	698
PAWS	61	437	553	857	541

Most of the liquid residues contained high amounts of acetic and butyric acids. Feed mixtures PAS and PAWS also produced significant amounts of succinic acid. The concentrations obtained is high enough that it might be economically feasible to use anaerobic digestion to produce large amounts of volatile fatty acids as they are more valuable as bio-based reagents than the methane gas.

4 CONCLUSIONS

The results from this study showed that the addition of lignocellulose substrates to pig manure during anaerobic digestion significantly increased the amount of biogas produced, but did not significantly increase the fraction of methane in the gas. High concentrations of valuable volatile fatty acids were found in the liquid residue which could be recovered to add value to the overall process. It can be concluded from the study that it is advantageous to add lignocellulose as substrate to the leachate of the gas it to be used for electricity generation, but not necessarily if a high methane content is required in the gas.

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7 LOGO SPACE