

Effect of Urea and NPK Fertilizer on the Anaerobic Digestion of Corn Stover (Corn Cob and Corn Sheath) for Biogas Production in a Batch Mode Bioreactor

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Abstract: *The effect of Urea and NPK Fertilizer on the anaerobic digestion of corn stover (Corn cob and Corn Sheath) for biogas production was evaluated. Four (4) bioreactors of 3L capacity were custom designed with plastic material for the anaerobic digestion of the corn stover. The corn cob (CC) and corn sheath (CS) were treated with urea (U) as follows: 3gU /65gCC; 6gU /65g CC; 9gU /65g CC; 3gU /65gCS; 6gU /65g CS and 9gU /65g CS in dry weight bases. Similar ratios of NPK fertilizer were used (3g/65g, 6g/65g and 9g/65g) to treat the corn cob and corn sheath. The bioreactors were separately charged with the different ratios, and were set-up in replicates. The methanogen source (inoculum) was freshly strained cow rumen liquor (20% final volume of bioreactor content). The anaerobic digestion, which was in batch mode, was operated for 31 days hydraulic retention time (HRT) at ambient temperature condition (26-35°C) and pH 5.33 - 8.0. Measurement of the daily biogas yield was by downward water displacement method. Comparative analysis (t- test $p \leq 0.05$) with the control indicated a significant difference in biogas yield in the test parameters: CC:U 65g/3g, CC:NPK 65g/9g, CS:U 65g/3g, CS:U 65g/6g and CS:NPK 65g/6g, with cumulative biogas yield of 2.18, 2.17, 3.29, 2.71 and 5.51 dm³, respectively. Computer aided regression analysis of the data from the test parameters that showed significant difference indicates that biogas yield is predictable as function of time. This implies the obvious possibilities of developing models for predicting biogas yield from different substrates as function hydraulic retention time (HRT). Supplementation of stover with urea and NPK fertilizer or other substrates rich in potassium and phosphorus holds a prospect in enhancing biogas production, and can be adopted in biogas technology for large scale production. However, further studies on the economics of the process are required.*

Keywords: Corn Stover, urea, NPK fertilizer, biogas, regression analysis

1. Introduction

For economic growth, social development, human welfare and improvement in the quality of life, energy input is of paramount importance. Energy inputs are needed in every sector of the economy-agriculture, industry, transport and domestic needs. Consequently, energy consumption in all forms has been on the increase across the globe. This growing consumption of energy has also resulted in many countries becoming increasingly reliant on fossil fuels such as coal, oil and gas [1].

These fossil fuels are not fulfilling the world energy demand. In addition, they are creating environmental problems like emission of greenhouse gases, and the increasing global temperature is an obvious threat [2]. Therefore, human beings are now challenged by the energy pinch and by the environmental contamination. This has led to emphasis on renewable energy sources and intensive researches in this direction [3].

Energy production from the organic matter by means of anaerobic digestion processes allow better waste management, preservation of the environment, development and diversification of energy resources [4].

Anaerobic digestion is a biological process known for energy recovery, especially in the form of biogas, from wastewater. The recovery of biogas as well as a reduction of

chemical oxygen demand (COD) in organic waste and waste stabilization is the main advantages of this process [5].

Biogas production by anaerobic digestion from biodegradable organic waste is increasingly seen as a viable renewable energy source. However, the efficiency of anaerobic digestion process is limited by a number of factors [6]. The qualitative and quantitative influence over the biogas production is strongly determined by the environmental conditions such as temperature, pH, biodegradable organic matter content of the raw material, the carbon to nitrogen (C/N) and carbon to phosphorus (C/P) ratio, retention time, volatile fatty acids (VFA), working pressure of the digester, presence of inhibitors, type of substrate, macro and microelements availability, particles size, etc. [7, 8].

In view of the compositional analysis of corn stover, it is very evident that it is rich in carbon than nitrogen. Under anaerobic digestion, this can lead to acidification in the bioreactor, thus, creating imbalance of pH (below 6.5), it leads to inhibition of methanogenic processes. This problem can be resolved by supplementing the substrates with a cheap and suitable nitrogen source, which give stability and enhances activity of methanogens [9].

The present study therefore, evaluates the effect of supplementing corn stover with different doses of urea and NPK fertilizer on biogas yield.

2. Materials and Methods

2.1 Preparation of the Substrates

The corn stover (corn sheath and corn cob) used in this study was collected from different sources at Obinze and other host communities of Federal University of Technology, Owerri, Imo State. The samples were sun-dried separately for 10 days until they were sufficiently dry. After drying, the samples were milled to finely reduced particle size, and subsequently stored in air-tight polyethylene bags to preserve the substrates. The urea was of laboratory grade (BDH). The NPK fertilizer was purchased from an open market at Umuapu, Ohaji LGA. It was finely ground before storage in an air-tight polyethylene bag.

Cow rumen fluid served as the inoculum, which is source of methanogenic bacteria. Rumen liquor from freshly slaughtered cow was collected in an air-tight glass container. It was strained with triple layer of cheesecloth; the liquor free from debris was stored air-tight to preserve the methanogens.

2.2 Determination of the Physico-chemical Composition of the Substrates.

The physico-chemical composition of the corn sheath and corn cob was determined by using the methods described by AOAC [10]. The total volatile solid (TVS), total solid (TS), moisture content, ash content, fat content, crude protein, fibre content, C: N ratio, fibre contents were determined.

2.3 Bioreactor Design and Operation.

The four (4) batch type bioreactors designed for the anaerobic digestion of corn stover were of three (3L) litre capacity plastic material. The experimental design and set-up were as described by Oporum *et al.*, [11]. The bioreactor has a thermometer and an outlet for gas in which three quarter inch (3/4) gas hose was tightly fitted and sealed.

The corn cob (CC) and corn sheath (CS) were treated with urea (U) as follows: 3gU /65gCC; 6gU /65g CC; 9gU /65g CC; 3gU /65gCS; 6gU /65g CS and 9gU /65g CS in dry weight bases [12]. The control contained only corn stover, corn cob and corn sheath.

Similar ratios of NPK fertilizer were used (3g/65g, 6g/65g and 9g/65g) to treat the corn cob and corn sheath. The bioreactors were loaded separately with the different ratios, and were set-up in replicates. The charged bioreactors were inoculated with freshly strained cow rumen fluid (20% final volume of the bioreactor content).

The anaerobic digestion was carried out under ambient temperature condition (26-35°C). Manual mixing of the bioreactor content at intervals was adopted to enhance contact between the digesting slurry and the microorganisms and avoid stratification of the slurry.

The gas collection was by water displacement method as described by Aragaw *et al.*, [13]. The volume of daily biogas yield is equivalent of the mean value of water displaced after

every 24hours. The hydraulic retention time was 31 days, during which changes in pH and temperature in the course of digestion were monitored with digital pH meter and the installed thermometer, respectively.

2.4 Biogas Analysis

The composition of the biogas produced in the study was determined. This was carried out at National Centre for Energy Research and development, University of Nigeria, Nsukka. The percentage composition of some of the constituent gases contained in the biogas was ascertained using biogas analyzer.

2.5 Data Analysis

The biogas yield in the different test parameters and the control were compared pair wise using students' T test implemented with Microsoft Excel 2003. Standard deviation and standard error (error bars) were applied in the analysis of generated data.

2.6 Regression Model of gas yield (GY) as Function of Hydraulic Retention Time (t)

Biogas yield was modeled as a function of time (t) using regression analysis with SPSS software, in those parameters where significant difference in biogas production was recorded.

$$GY = a + bt + \epsilon$$

Where: **a** = the unstandardized coefficients/constant which represents the value of

GY when t equals Zero.

b = the standardized coefficient which represents the value t per unit rise in GY.

ϵ = the error estimate in the regression model

Ra^2 : The values of Ra^2 for models produced by the regression procedure range from 0 to 1. Larger values of Ra^2 indicate stronger relationships between the gas yield and HRT (days). R squared adjusted (Ra^2) is the proportion of variation in the dependent variable explained by the regression model. The sample R squared adjusted (Ra^2) tends to optimistically estimate how well the model fits the parameters.

P-value: If the significance value of the F-ratio statistic is small (Less than 0.05) then the independent variables of HRT (days) does a good job explaining the variation in the dependent variable of Gas Yield.

3. Results and Discussion

The physicochemical characteristics of the corn cob and corn sheath are shown in Table 1. The volatile solids (VS) content of corn cob and corn sheath are 84.64% and 86.39%, respectively. This indicates that these substrates are sufficiently rich in organic solids that can be digested under anaerobic condition and converted to biogas. The result also revealed a high C/N ratio in both corn cob (60:1) and corn sheath (56:1). It has been posited from previous researches that in anaerobic digestion process, the microbial populations utilize between 25 to 30 times carbon faster than nitrogen. Therefore, organic materials which are high in

carbon content can be blended with those that have low nitrogen or vice versa to attain the desired carbon to nitrogen ratio (C/N) of 30 [14].

Carbon to nitrogen ratio (C/N) is one of the most important factors that influence anaerobic digestion and biogas production from different substrates, and this makes it a vital parameter that must be put into consideration in enhancing biogas production from feed stocks [15]. This underscores the necessity to maintain proper composition of the feedstock for efficient plant operation so that the C/N ratio of the feeds undergoing anaerobic digestion remains within desired range.

Shown in Figure-1 are plots of the mean values of the daily biogas production, the corresponding pH changes against the hydraulic retention time (HRT), and the pattern of anaerobic digestion of corn cob with different ratios of urea. In the bioreactor charged with 3g urea/ 65g corn cob, biogas production started on the very first day though in a very low volume. A sharp increase in biogas production from 18.45 ml in day 3 to 172ml in day 4 at a pH 6.82 was observed. Peak of biogas production was noted in day 6 (180.90ml) at pH 6.72. Biogas production dropped below 100ml on day 17, when the pH reduced below pH 5.35. Cumulative biogas yield of 2.18 dm³ (115.32% increase in biogas) and 68.45% methane yield was recorded, while the control was 1.02dm³ and 59.01 % methane content.

The bioreactor charged with 6g urea/ 65g corn cob recorded a peak biogas yield on day 18, with a mean value of 208.60ml at pH 6.70. Though biogas production started in day 1, it dropped down to zero in days 4 through day 8. The pH fluctuated between pH 8.0 to 6.32 throughout the 31 days hydraulic retention time. The cumulative biogas produced was 1.65dm³ (62.61% increase in biogas) and 59.96% methane yield. Similar report was made by Pound *et al.*, [12] in which the addition of urea to pressed sugar cane stalk had the effect of increasing pH, and substantially reducing the length of the lag phase of the cumulative biogas production curves.

In the bioreactor with 9g urea/65g corn cob, though the treatment stabilized the pH in the range ideal for biogas production, very low activity and performance in terms of biogas production (0.10 dm³) was recorded. This dose showed inhibitory effect on biogas production, and could be attributed to high ammonia generation in the bioreactor which may have negatively affected the performance of the methanogens. Flammability test revealed that flammable biogas production started on the 4th day in 3g/ 65g urea to corn cob, 14th day in 6g/65g and 11th day in 9g/65g urea to corn cob.

Statistical analysis (t- test $p \leq 5\%$) was used to compare the different treatments with control. Treatment with 3g/65g urea to corn cob showed a significant difference in biogas production with 2.18dm³ cumulative yield which amounts to 115.32% increase in biogas production. In the bioreactor charged with 6g urea/65g corn cob, biogas production increased by 62.61% (1.65dm³). Previous studies on the effect of supplementation of pineapple pulp waste with varying concentrations of urea showed that 2 % urea is the

most optimum for production of biogas which yields 19 % more biogas than the control [8].

Presented in Figure-2 is the pattern of anaerobic digestion of corn cob with different ratios of NPK fertilizer. The means values of biogas produced and the changes in pH were plotted against the hydraulic retention time. In the bioreactor charged with 3gNPK/65g CC, biogas production started on day 1, reached its peak of day 3 with gas volume 399.25ml at pH 5.20. Biogas production started staggering by day 5 with no gas production from day 8 to day 13 and finally falls to zero on day 31. This ratio did neither improve biogas yield nor pH of the digesting slurry. The cumulative biogas produced throughout the digestion period is 0.79dm³, which is lower than the control, 1.02dm³.

In the ratios 6gNPK/65g CC and 9gNPK/ 65g CC, the lag phase lasted for one (1) day before the commencement of gas production. The cumulative yield (Table 2) and the corresponding percentage increase in biogas in the different doses, 6g/65g and 9g/65g NPK to corn cob (CC) are 1.28dm³ (26% increase) and 2.17dm³ (114.39% increase), respectively.

Comparative statistical analysis of the mean values of daily biogas yield indicated that 9g/65g of NPK to corn cob significantly ($P \leq 5$) enhanced biogas production. The result of the standard deviation showed a very low variation in the different bioreactors, and the data are close to the expected values, and was used to introduce error bars in the graph.

Figure-3 shows the anaerobic digestion pattern of corn sheath with different ratios of urea, the daily biogas production and corresponding changes in pH. Combustible biogas production started on day 5 in bioreactor with 6gU/65gCS and day 11 in bioreactor with 9gU/65g CS.

Statistical analysis (t test $p \leq 5\%$) showed that CS65g/U3g (3.29dm³) and CS65g/U6g (2.71dm³) were significantly different in biogas production. The percentage increase in biogas yield is 174.26% for CS65g/U3g, 126.41% for CS65g/U6g and 32.55% for CS65g/U9g. The results obtained from this study are in conformity with the reports of Getachew [16]. He studied the effect of adding urea on biogas (methane) potential of selected fruit wastes and observed that the ultimate biogas yield from using avocado, banana, and mango fruit wastes as substrate is; 0.48, 0.57, 0.53 l/g VS without adding urea and 0.76, 0.82, 0.82 l/g VS adding urea with a statistically significant difference (p -value; 0.006 for avocado, 0.029 for banana, and 0.007 for mango FW at 95% Confidence Interval respectively). Thus, urea addition significantly improved biogas yield. Membere *et al.*, [17] in a similar study evaluated a computational model for biogas production as a function of time using urea, cow and horse dung as inoculums. Organic Fractions of Municipal Solid Waste (OFMSW) was co-digested with the inoculums anaerobically under ambient temperature condition. The results showed that the first order kinetic constant of -0.0114 and Short Term Anaerobic Biodegradability Index (STABI) of 5.4495 for Digester A, containing 30 g of urea and 10 g of food waste; had the highest yield of biogas with cumulative volume of 389.7 ml and an R² value of 0.9934.

The anaerobic digestion pattern, biogas yield and pH changes in the bioreactors containing 3gNPK/65g CS, 6gNPK/65gCS and 9gNPK/65gCs are presented in Figure-4. The cumulative biogas yield is 1.83dm³(55.33%), 5.51dm³(359.84%) and 1.60dm³(33.56%), respectively. It was noted that all the treatment conditions remarkably enhanced biogas production. Statistical (t-test $p \leq 5\%$) analysis showed a significant difference in biogas production in 6gNPK/65g CS.

So far there is very limited academic literature available on supplementing organic substrates with NPK fertilizer. The results indicate that in addition to C: N ratio, other macronutrients such as potassium and phosphorus etc. are necessary for enhanced biogas production. In addition to an organic carbon and energy source, anaerobic bacteria appear to have relatively simple nutrient requirements, which include nitrogen, phosphorus, magnesium, sodium, manganese, calcium, iron and cobalt [18]. Nutrient levels should be sufficient for the optimal concentrations needed by the methanogenic bacteria, since these are the most severely inhibited by slight nutrient deficiencies. Nutrient additions are often required in order to permit growth in digestion of industrial wastes and crop residues [19].

Regression analysis of gas yield as a function of time (t) in test parameters that showed significant difference in biogas

yield using SPSS software(computer aided)indicates that the biogas yield is highly correlated to time (t) except for corn sheath/urea (65g/6g) where the $Ra^2 = -3.40$ and p -value = 0.932(Table3). Anaerobic digestion of different substrates has been viewed as function of time; this relationship was quantified using regression analysis. The result of the analysis indicated that gas yield can be predicted as a function of time; however other conditions also come to play. Similar report was made by Ofoefule *et al.*, [20]. The mathematical models derived by these researchers, using computer aided regression analysis were used to evaluate biogas production from animal wastes as a function of time and total microbial viable count. The results strongly indication that biogas yield can be predicted based on hydraulic retention time and total microbial viable count.

The result of compositional biogas analysis is shown on Table 4. These results indicate that the treatment appreciably enhanced the methane yield and hence improved biogas quality, except in the ratio, 65gCC/6gU where the methane content is almost the same as that of the control. This result agrees with the report of a previous study on the supplementation of cassava tubers with urea for biogas production which yielded biogas with 67.92% methane content [21].

Table 1: Compositional (Proximate) Analysis of the Substrates

Substrate	Moisture content (%)	Ash (%)	Crude protein (%)	Crude Fibre (%)	Nitrogen (%)	Organic Carbon (%)	C/N Ratio (%)	TS (%)	VS (%)
Corn Cob	9.58	5.78	7.61	34.66	0.96	57.81	60.21	90.39	84.64
Corn Sheath	9.63	3.88	20.79	27.70	0.88	48.32	56.00	90.35	86.39

Table 2: Cumulative Biogas Yield and Percentage increase from the Treatment of Corn Stover with Urea and NPK fertilizer at Different ratios

Substrate/unit	Cumulative Yield (dm ³)	% increase in Biogas
Corn Cob (Control)	1.02	-
Corn Sheath(Control)	1.20	-
CC:U 65g/3g	2.18	115.32
CC:U 65g/6g	1.65	62.61
CC:U65g/9g	0.10	-
CC:NPK 65g/3g	0.79	-
CC:NPK 65g/6g	1.28	26
CC:NPK65g/9g	2.17	114.39
CS:U65g/3g	3.29	174.26
CS:U65/6g	2.71	126.41
CS:U65g/9g	1.59	32.55
CS:NPK65g/3g	1.83	52.33
CS:NPK 65g/6g	5.51	359.84
CS:NPK 65g/9g	1.60	33.56

Table 3: Regression Parameters of the different Ratios

Substrates	a	b	ϵ	Ra^2 (%)	P-value
Corn Cob (Control)	93.97	-0.575	1.014	30.7	0.001
Corn Sheath (Control)	120.81	-0.483	1.729	20.7	0.006
Corn cob/Urea (65g/3g)	130.09	-0.586	0.961	32.0	0.001
Corn cob/NPK (65g/9g)	138.55	-0.597	1.184	33.4	<0.001
Corn Sheath/Urea (65g/3g)	281.59	-0.690	2.291	45.8	<0.001
Corn Sheath/Urea (65g/6g)	89.10	-0.016	0.904	-3.40	0.932
Corn Sheath/NPK (65g/6g)	382.62	-0.504	5.532	22.8	0.004

Table 4: Compositional Biogas Analysis

Parameters/unit	Biogas Constituents.		
	Methane (CH ₄)	Carbon(IV) oxide (CO ₂)	Carbon(II) oxide (CO)
Corn Sheath	61.80	34.50	1.78
Corn Cob	59.01	37.00	2.05
65gCC/3gU	68.45	29.80	1.45
65gCC/6gU	59.96	37.43	1.64
65gCS/3gU	72.60	24.50	2.30
65gCS/6gU	70.00	27.13	1.06
65gCC/6g NPK	68.31	30.22	1.15
65gCC/6gNPK	73.10	24.15	1.84
65gCS/3gNPK	69.58	28.44	1.32
65gCS/6gNPK	73.46	24.35	1.65
65gCS/9gNPK	62.83	34.66	1.42

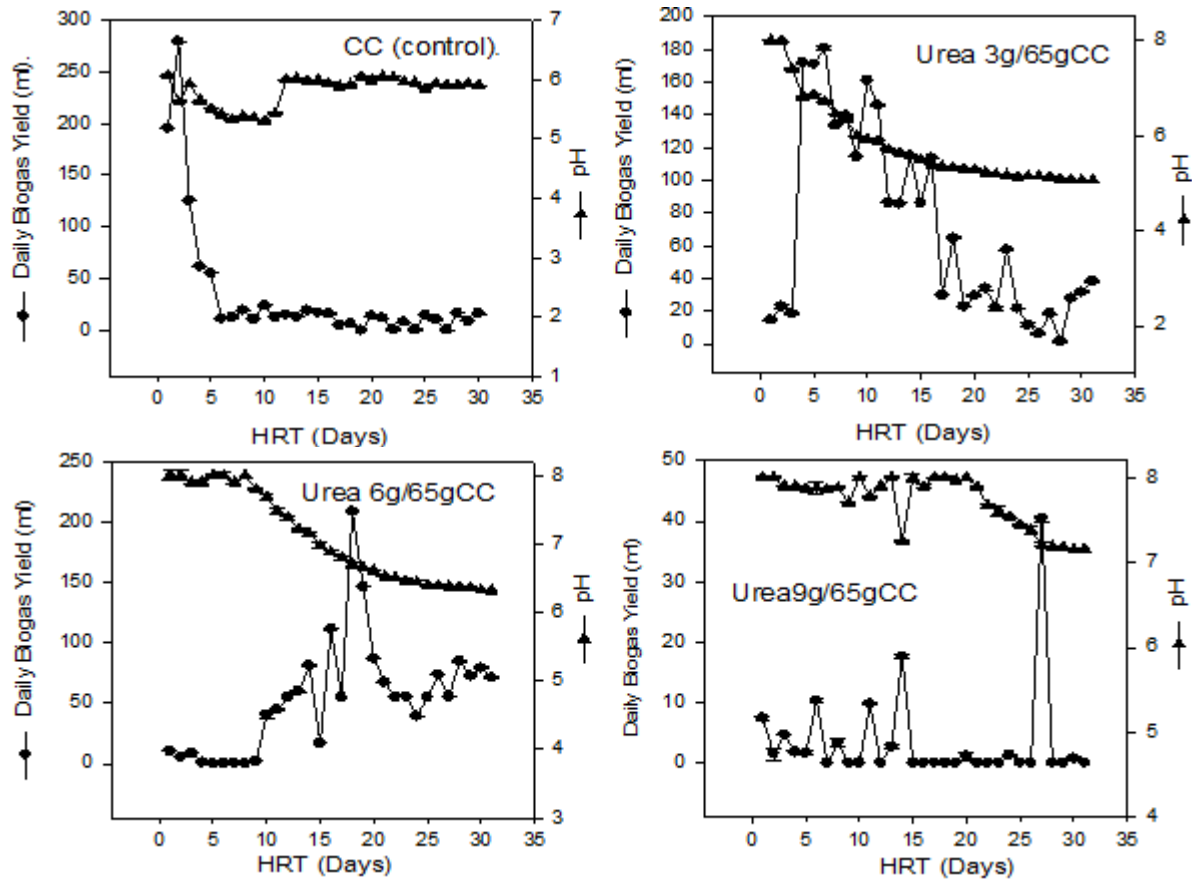


Figure 1: The anaerobic digestion pattern of corn cob with different ratios of urea and daily biogas production, and corresponding pH changes

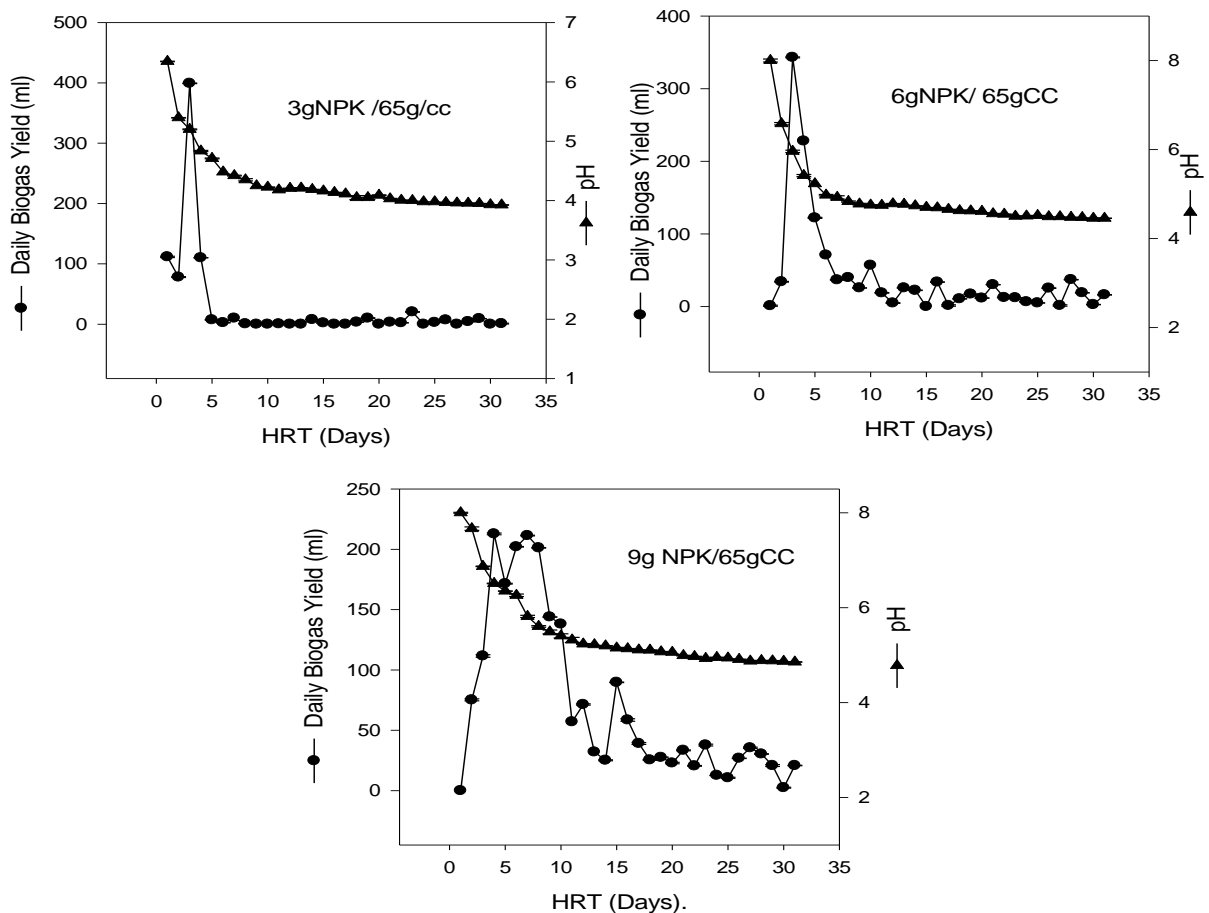


Figure 2: The anaerobic digestion pattern of corn cob with different ratios of NPK fertilizer and daily biogas production, and corresponding pH changes.

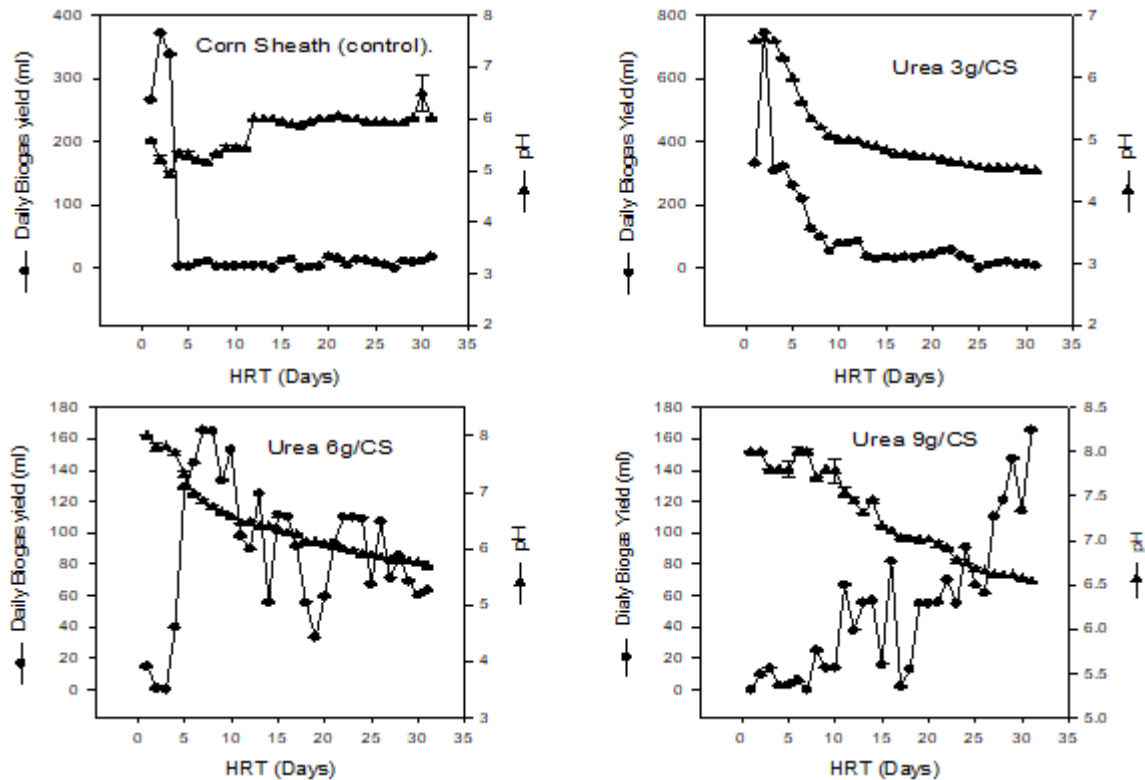


Figure 3: The anaerobic digestion pattern of corn sheath with different ratios of urea and daily biogas production, and corresponding pH changes

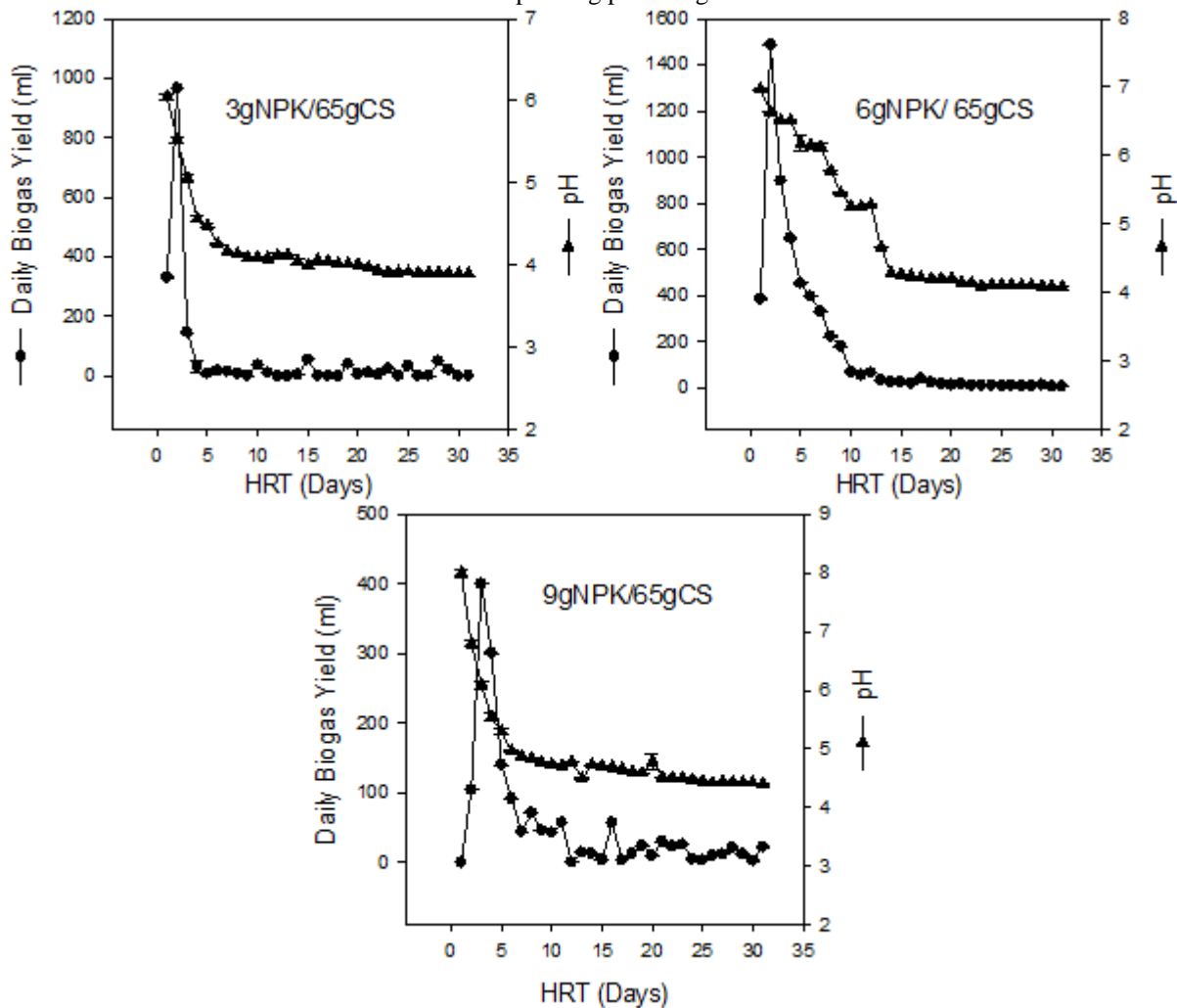


Figure 4: The anaerobic digestion pattern of corn sheath with different ratios of NPK fertilizer and daily biogas production, and corresponding pH changes

4. Conclusion

Corn stover (corn sheath and corn cob) requires one form of treatment or the other to optimize their biogas production potential. The results of this study indicate that in addition to C/N ratio, other macronutrients such as potassium, phosphorus etc. are necessary for enhanced biogas production. Supplementation of corn stover with varying ratios of urea and NPK fertilizer not only significantly enhanced biogas production, but also appreciably increased the methane content of the biogas. Enrichment of corn sheath with NPK fertilizer or other substrates rich in potassium and phosphorus holds a prospect in enhancing biogas production, and can be adopted in biogas technology for large scale production of biogas. However, further studies on the economics of the process are required.

Computer aided regression analysis of the data from the test parameters indicates that biogas yield is predictable as function of time. This implies the obvious possibilities of developing models for predicting biogas yield from different substrates as function hydraulic retention time (HRT).

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