

Thermochemical Pretreatment of Water Hyacinth for Improved Biomethanation

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Received September 21, 1992; Accepted January 25, 1993

ABSTRACT

Water hyacinth was subjected to various thermochemical pretreatments and used as a substrate in anaerobic digestion for biomethanation. Results indicate that the pretreatment increased the solubility of biomass and improved gas production. Best results were obtained when water hyacinth was treated at pH 11.00 and temperature 121°C. Severe treatment conditions showed a negative effect, especially on methanogenic bacteria caused by toxic compounds produced during treatment.

Index Entries: Pretreatment; biogas; water hyacinth; energy; anaerobic digestion.

INTRODUCTION

In India, many bodies of water have been damaged because of the excessive growth of aquatic weeds, particularly water hyacinth (*Eichhornia crassipes*), to the extent that they are of no further use. Water hyacinth (WH) has grown at an alarming rate and to such explosive proportions that all efforts to bring it under control have failed. Today, its utilization is considered an important part of weed management. Among possible uses, anaerobic digestion of water hyacinth resulting in the production of biogas, a valuable source of energy, has attracted much attention in the recent

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past (1–4). WH has a high productivity coupled with an excellent pollutant removal and methane generation potential that makes it amenable to utilization in integrated pollution control and energy conversion systems in rural areas. Cattle dung (CD) has so far been the major resource for biogas production (5–7). In recent years WH has come to be used as a replacement for CD, mainly because of the limited availability of the latter (3,4,8). In practice, however, a problem arises because of the nature of the organic content in this material, and digester performance has not been consistently good. Our earlier studies showed that WH:CD used in the ratio of 7:3 on a dry weight basis gives a high production of biogas with enriched methane content (8). However, there is still a growing interest in maximizing extraction of methane for energy recovery from WH so that farmers will be more likely to adopt this process. Therefore, further process improvements are needed.

It has been reported that dilute alkaline solutions of hydrogen peroxides at pH 11.5 solubilized half of the lignin and most of the hemicellulose present in agricultural residues at 25°C, which result in improved biomethanation (6,9). Heat treatment of cattle waste has shown to increase biogas production (10). Yang and Chan (1985) developed a novel process for treating municipal solid waste based on the chemical solubilization of cellulose (11), and retention time of anaerobic digestion of municipal solid waste containing a high proportion of cellulose was reduced significantly. In general acid and alkaline treatment of solid feeds at higher temperature have shown to be effective in improving digester gas yields (12–14).

A major contributor to biogas production from WH is the rate of lignocellulose hydrolysis, and one possible means of increasing methane production efficiently is the delignification of WH so as to make substrate accessible for microbial attack. WH, a lignocellulosic waste material, can be pretreated chemically or physically to increase its biotechnological substrate value. No detailed study, however, seems to have been done so far on the thermochemical pretreatment of WH. Therefore, it was felt necessary to study the effect of thermochemical pretreatment on WH with the objective of improving the performance stability and the rate of decomposition, with improved gas production.

MATERIALS AND METHODS

Resources

WH was obtained locally, it was dried at 60°C, and powdered to 50 mesh. Fresh CD was always obtained locally. All the chemicals used were of analytical grade.

Pretreatment

In a thermochemical pretreatment 50 mesh WH powder in a 10% (w/v) slurry was treated at temperatures of 50, 100, and 121°C (with steam) for each pH. The pH values used for this study were 1, 3, 5, 7, 9, 11, and 13. pH Values were adjusted by adding appropriate quantity of either HCl or NaOH. All treatments were given for 1 h. After the treatments, samples were cooled to room temperature and pH was adjusted to 7.0 using HCl or NaOH and they were used as such for loading into the digester. Care was taken to adjust total solid (TS) as 7% (w/v) before loading into the digester.

Anaerobic Digestion

Several bench scale anaerobic digesters were used. Each vessel consisted of a 10 L glass reaction bottle, having a working volume of 6 L and containing 7% (w/v) of TS. The digesters were intermittently stirred with magnetic stirrers and maintained at $37 \pm 1^\circ\text{C}$. Gas was collected and measured by displacement of acidified saturated salt solution, making needed corrections for atmospheric pressure and temperature. The digesters were fed on a semicontinuous basis: once/d using a freshly prepared mixture of treated WH biomass (for treated sets containing mixture of treated WH and CD in the ratio of 7:3 (w/w)) or untreated WH powdered (50 mesh) (for control set containing untreated WH and CD in the ratio of 7:3 (w/w)) and CD in the ratio of 7:3 (w/w), with a retention time (RT) of 8 d (where loading rate was 8.75 g TS/L of digester/d). This was found to be most suitable from our initial study (8). Prior to feeding an equal quantity of sludge was withdrawn from the bottom of the digester.

A fresh digester was always started by preparing a mixture of the treated or untreated WH and CD in the ratio of 7:3 (w/w) to give a final TS concentration of 7% (w/v) and using a 10% inoculum from the running biogas digester of the same type. A steady state condition was decided upon through constant mean gas production rate and also from effluent BOD and COD values remaining almost constant. Experiments were carried out in triplicate and average data are presented.

Analysis

Gas composition was analyzed with a CIC gas liquid chromatogram with stainless steel Chromosorb 2 column and thermal conductivity detector (7). Helium served as the carrier gas for methane and carbon dioxide. Identification and percentage of methane and carbon dioxide were based on comparison of retention time and peak areas of unknown with standard amount of two gases.

Table 1
Major Organics in Water Hyacinth

	W Percent dry solids
Cellulose	17.8
Hemicellulose	43.4
Lignin	7.8
Crude protein	11.9
Ash	20.2

Feed and effluent slurry were routinely analyzed for pH, volatile acids, biological oxygen demand (BOD), chemical oxygen demand (COD), TS, and volatile solids (VS) as per standard procedures (15).

RESULTS AND DISCUSSION

Major organics in WH have been analyzed and reported in Table 1. Like other biomass residues, it is lignocellulosic in chemical composition and contains a considerable amount of lignin in association with cellulose and hemicellulose. Cellulose and hemicellulose can potentially be fermented. The degree of conversion is dependent on the degree of their association with lignin, a natural binder that in itself is virtually totally recalcitrant. Therefore, different types of thermochemical pretreatments of WH were carried out.

Table 2 summarizes the effect of various pretreatments on chemical composition of WH slurry prior to feeding the digesters. The percentage solubilization as measured by the ratio of SCOD (Soluble COD) to TCOD (Total COD) is also presented in Table 2. The results indicate that heat treatments as low as 50°C produce an increase of 46.77% (at pH 13.0) on COD solubility. The treatment at 121°C increased COD solubility by 66.65% (at pH 13.0), indicating that solubilization of organic matter increases with heat treatment (10). Acid (HCl) and alkali (NaOH) addition showed different effects according to temperature. In general the alkali addition showed a more pronounced effect than the acid. Therefore, when the WH biomass was treated at pH 13.0 and 121°C, the percentage of COD solubilization was 66.65%. The alkali effect was probably a result of the solubilization of lignin. This treatment is also responsible for delignification; lignin would otherwise be a major obstacle. The compositional changes in the treated solids can be advantageous or disadvantageous from the digestibility point of view. The solubilization of lignin constitutes advantages in the sense that it liberates the remaining solid phase carbohydrate and increases its porosity, on the other hand, the soluble lignin derivatives may exert toxic effects (14).

Table 2
Effect of Thermochemical Pretreatments
on COD Solubilization of Water Hyacinth

Treatment temperature		TCOD, g/L	SCOD, g/L	Percent COD solubilization	Volatile acids, g/L
Control ^a	pH	51.20	8.19	16.00	1.50
50	1.0	55.20	20.18	39.43	1.78
	3.0	54.43	18.57	36.27	1.43
	5.0	51.37	16.32	31.88	1.28
	7.0	49.49	13.47	26.32	1.02
	9.0	50.12	17.54	34.26	1.45
	11.0	51.20	22.00	42.95	1.62
	13.0	54.60	23.94	46.77	1.82
100	1.0	52.76	26.42	51.61	1.91
	3.0	53.31	23.94	46.77	1.64
	5.0	49.80	21.73	42.45	1.35
	7.0	46.70	18.58	36.29	1.15
	9.0	46.70	24.72	48.30	1.70
	11.0	49.88	27.66	54.03	2.20
	13.0	49.88	30.55	59.67	2.83
121	1.0	50.30	30.96	60.48	2.32
	3.0	51.41	27.24	53.22	2.17
	5.0	51.27	22.29	43.54	1.96
	7.0	51.91	19.60	38.30	1.45
	9.0	52.18	26.96	52.66	2.32
	11.0	52.00	29.94	58.48	3.21
	13.0	51.28	34.12	66.65	4.10

^a Ten percent (w/v) slurry of water hyacinth in water using powdered WH (dried at 60°C and powdered to 50 mesh).

The biodegradability of WH biomass was tested in semicontinuous anaerobic fermentation in terms of its gas production and its methane content. Steady-state performance efficiency is shown in Fig. 1, which shows enhanced gas production with decreasing pH and increasing temperature, reaching maximum at pH 3.0 and 121°C. Pretreatment of WH by acid did not enrich methane content in the digester gas. This may be because acidic treatment improves the acid production phase. This is also supported by a higher volatile acid content in the steady-state pretreated WH digesters.

In general process stability is evidenced by lower volatile acids (5,7,16). However, in this system, in spite of increase in volatile acids, the process seems to be highly favorable with high yield. During the steady-state period, the mixed population develops the ability to convert particular organic molecules to methane (17) through population selection or enzyme induction.

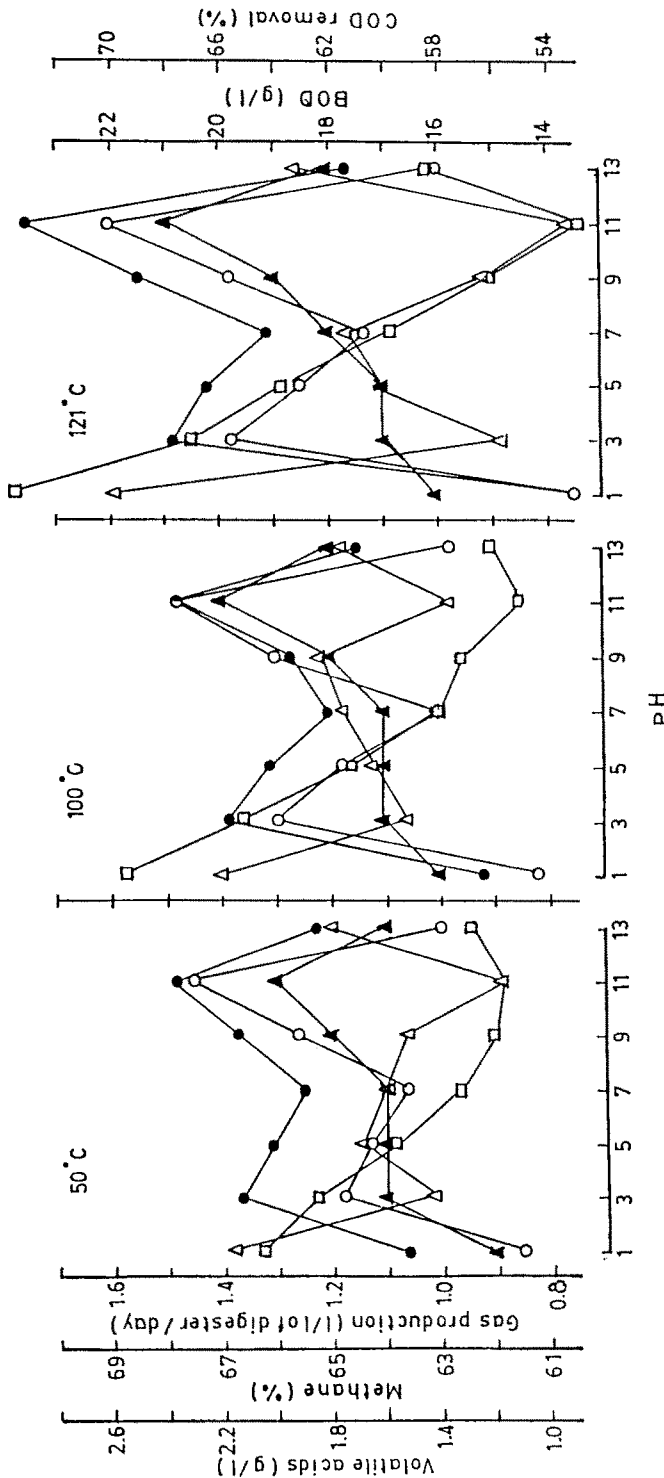


Fig. 1. Anaerobic digestion profile of water hyacinth (treated) cattle dung. Operating conditions; temperature, $37 \pm 1^\circ\text{C}$; retention time, 8 d; loading rate, 8.75 g TS (WH : CD, 7 : 3, W/W)/L of digester/d. Control, untreated WH with CD (7 : 3, W/W), COD-27.2 g/L; BOD-17.3 g/L; percent COD removal, 62.01; Gas production, 1.01 L/L of digester/d, CH_4 , 64%. Symbols: O, Gas production; ▲, Methane; □, BOD; △, Volatile acids; ●, COD removal.

The acidic thermochemical treatments have a positive effect on acid forming bacteria. The volatile acid production was more than that observed for the control (with untreated WH and CD 7:3, w/w). The methane content was between 62–64% for the majority of experiments. The methane content of the biogas indicated a well buffered system.

With further decreases in pH during pretreatment (pH 1.0), though improving the volatile acid production, the overall process was inferior in terms of total gas production and its methane content. Treatment at pH 1.0, at all temperatures, caused a slight arrest in gas production. This may be because of the accumulation of toxic products during treatment or by the presence of a high concentration of chloride caused by HCl addition during treatment (18). This can be attributed to the poor performance of methane bacteria.

A trend of enhanced gas production with increased pH and temperature during treatment is evident from Fig. 1. Maximum enhancement (of over 60%) was achieved with the treatment at pH 11.0 at 121°C. In addition, this treatment was also responsible for higher methane content in the digester gas. The control digester, which contained untreated WH, gave 1.01 L/L of digester/d with 64% methane. Alkali treatment showed greater increase in digestibility at higher temperature and was found to be advantageous to anaerobic fermentation for higher yield.

Volatile acids contents were low in treated digesters (0.87 g/L) as compared to untreated digester (1.35 g/L). It appears that alkaline treatment did enhance the methane forming step of the digestion process, which often involves the degradation of fatty acids, in addition to solubilization of WH biomass. However, higher alkaline treatment at all temperatures were found to be detrimental to the digester and may be caused by inhibition or toxicity raised by high sodium ion concentration (14) or the production of toxic aromatic substances as a result of lignin degradation. This needs further investigation.

Process performance can also be judged by BOD. It was found that under acidic or alkaline treatment BOD values were low, indicating greater biodegradation (19). This also indicated that microbial degradation of organic matter was at a higher rate in the treated WH digester than in control (BOD 17.2 g/L). Figure 1 also gives the data on the percent of COD removal. This parameter is important because the values suggest bacterial efficiency (19), and show that treatments improve bacterial efficiency, thereby increasing biodegradation.

ACKNOWLEDGMENTS

The author thanks DNES, New Delhi, India for financial support.

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