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RESEARCH ARTICLE

Biomethanation of acid pretreated biofuel process stillage for enhanced energy

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Abstract

Development of sustainable energy systems based on renewable biomass feedstock is now a global effort. Fuels produced from biomass have the potential to reduce reliance on petroleum resources and reduce greenhouse gas emissions. Biofuels obtaining from coproduced residues remains one of the major challenges in full scale opera- tions. This study investigated the potential of an anaerobic digestion system to convert the stillage obtained from pearl millet based lignocellulosic biofuel production. Biomethanation experiment study was conducted in CSTR using acid pretreated pearl millet based biofuel stillage upto 30 days. Using SAS software the multi colinearity was identified among different parameters of pH, TS, VS and VFA profile were analysed for identifying the major factor impacting biogas production. The initial parameters of stillage were pH 6.8, VS 978 $mg.l^{-1}$, TS 988 $mg.l^{-1}$ and VFA 802.44 $mg.l^{-1}$. The maximum biogas production 0.17 L was obtained at neutral pH of 7.4 on 16^{th} day with respect to reducing the VFA 9.45 m $mol.l^{-1}$ acetate, VS 954 $mg.l^{-1}$ and TS 973 $mg.l^{-1}$ after which there was reduction in the gas production due to alkaline pH even though TS, VS and VFA were reduced.

Keywords: lignocellulosic biomass, Acid pretreatment, Stillage, Anaerobic digestion and Continuous Stirred Tank Reactor.

Introduction

The hunt for alternative sources of energy gen- eration that are inexpensive, ecofriendly, renewable and can replace fossil fuels is on, owing to the increas- ing demands of energy. One approach in this direction is the conversion of plant residues into biofuels where- in lignocellulose, which forms the structural frame- work of plants consisting of cellulose, hemicellulose and lignin, is first broken down and hydrolyzed into simple fermentable sugars, which upon fermentation form biofuels such as ethanol (Morales *et al.*, 2015) Methane is an energy-rich component that is formed as the end product during the anaerobic decomposi- tion of organic matter, such as domestic slurries and residues coming from food processing manufactories. Among many different materials that can be used for biogas production, lignocellulose-rich materials, such as plant wastes, and protein-rich materials, such as animal manure, are highly promising due to their high methane potential (Divya *et al*., 2015) It is estimated that the world lignocellulosic biomass fixes tenfold the solar energy amount per year compared to the total yearly energy demand of all humans. This study investigated the potential of using anaerobic diges- tion to convert acid pretreated stillage into biogas.

Methods

Sample preparation

The pretreatment was carried out using TS 7.5 % (w/v) of pearl millet biomass immersed in a 12 % or- thophosphoric acid solution. The hydrothermal treat- ment was done in the reactor at a 6 bar pressure with temperature of 170˚C for 40 min. The resulting solid fraction was dried at 40˚C in an oven. Enzymatic sac- charification was done using cellulase enzyme at 40 FPU/g of cellulose (Mishra *et al*. 2011). Fermentation was carried out by *Saccharomyces cerevisiae* and eth- anol was quantified in a GC. The stillage obtained af- ter ethanologenic fermentation was used as substrate for biogas production.

Experiment setup

Biomethanation study was conducted in a Continuous stirred tank reactor (CSTR) with work- ing volume of 1.5 L capacity of acid pretreated still- age for a period of 30 days. The reactor was started up with 5 % cowdung slurry to stabilise the micro- bial and methanogenic activity inside the reactor with continuous supply of N_2 gas. Biogas production measured alternate days using water displacement method, methane content quantified using GC- FID poropak-Q column and the TS, VS and VFA measured with respective gas production. The reactor pH was measured in the displaying unit of the reactor. Using Statistical analysis system (SAS)-9.4version software linear regression analysis was done and major factor influencing on biogas production was identified. High *F* and *R2* values and low P value for biogas yield indi- cated the model predictability.

Results and discussion

The initial parameters of stillage were as, pH 6.8, VS 978 mg.l^{-1}, TS 988 mg.l^{-1} and VFA 802.44 mg.l^{-1}. Themaximum biogas production172 ml was obtained at neutral pH of 7.4 on 16th day with respect to reducing the VFA 9.45 m.mol.l^{-1} acetate, VS 954 mg.l^{-1} and TS973 mg.l^{-1} after which there was reduction in the gas production due to alkaline pH even though TS, VS and VFA were reduced.

During the first 10 days of biomethanation pro- cess, the gas production in the digester slightly in- creased to about 0.25 -0.63 l biogas. The pH ranged between 6.8–7.2 and the VS, TS and VFA contents decreased gradually. The gas production reached maximum (0.17 l) at 16th day with a pH of 7.4. As the process progresses, the volatile fatty acids were me- tabolized and the pH gradually increased to the suffi- cient buffering capacity (neutral pH) necessary for the production of biogas. Moreover, both acidogenic and methanogenic microorganisms have their optimal pH for metabolism, but the methanogens are highly pH sensitive and thrive optimally within the pH range of 6.8-7.6. This explains the high flammability rate of the biogas in this study, at pH 7.4 on the 16th

day of the di- gestion process owing to the increase in methanogen- ic activity of the digester system (Babaee *et al.,* 2013*).*

However, after 16 days of operation the efficien- cy of the process deteriorated with a considerable decrease in gas production indicating process insta- bility. Initially, the pH was maintained around 7.4 but continued to increase after 20 days of operation, and then kept varying between 7.58 and 8.12. Because of the alkaline pH the methane content of the gas de- creased to about 50%. So it was evident that though the TS, VS and VFA contents reduced constantly, the pH kept increasing thus negatively affecting the bio- gas production.
The gas production started to increase with increase in the pH and reached maximum gas pro- duction 0.17 L at the pH of 7.4. The gas production declined due to alkaline pH. (Fig 1a). The first 10 days of the VS content inside the reactor decreased from 978 – 973 $mg.l^{-1}$ with respective gas production and the VS continuously decreased upto 870 $mg.l^{-1}$. (Fig 1b). The TS content of the reactor gradually de- creased from 988- 957 $mg.l^{-1}$.(Fig 1c). The initial value of VFA content was 802 $mg.l^{-1}$ and it reduced upto 50 % during the whole anaerobic digestion process and the final value of VFA was 433 $mg.l^{-1}$. (Fig 1d).

The characteristics of the substrate and pres- ence of alkaline pH affect the microbial succession of anaerobic degradation and subsequent methane pro- duction. During methane production of organic mate- rial, four main metabolic groups have been identified: hydrolytic bacteria, fermentative bacteria, acetogenic bacteria and methanogens. Activity of methanogens and acetogens, which perform the last degradation steps, is essential for efficient and stable process. In- hibitory compounds can negatively affect the growth and activity of the microorganisms performing the last degradation steps, resulting in accumulation of vola- tile fatty acids (VFA) and a possibilities of subsequent increase in pH, which inhibits the entire degradation and may reduce the efficiency of biomethanation(Wang *et al*., 2009).

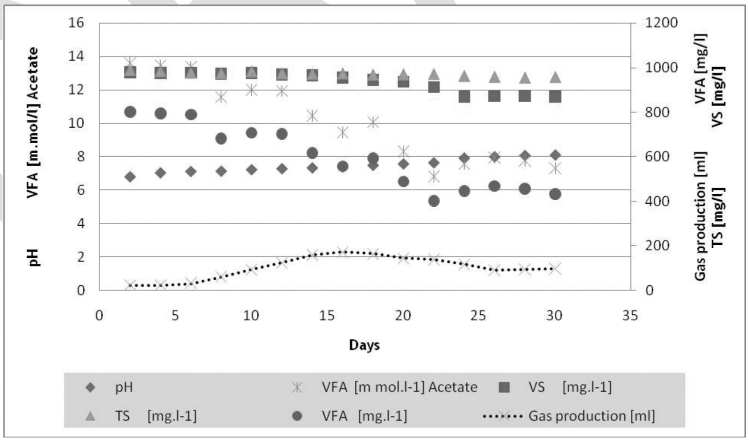

Figure 1.Physico-chemical parameters of CSTR biomethanated acid pretreated pearl millet biomass stillage

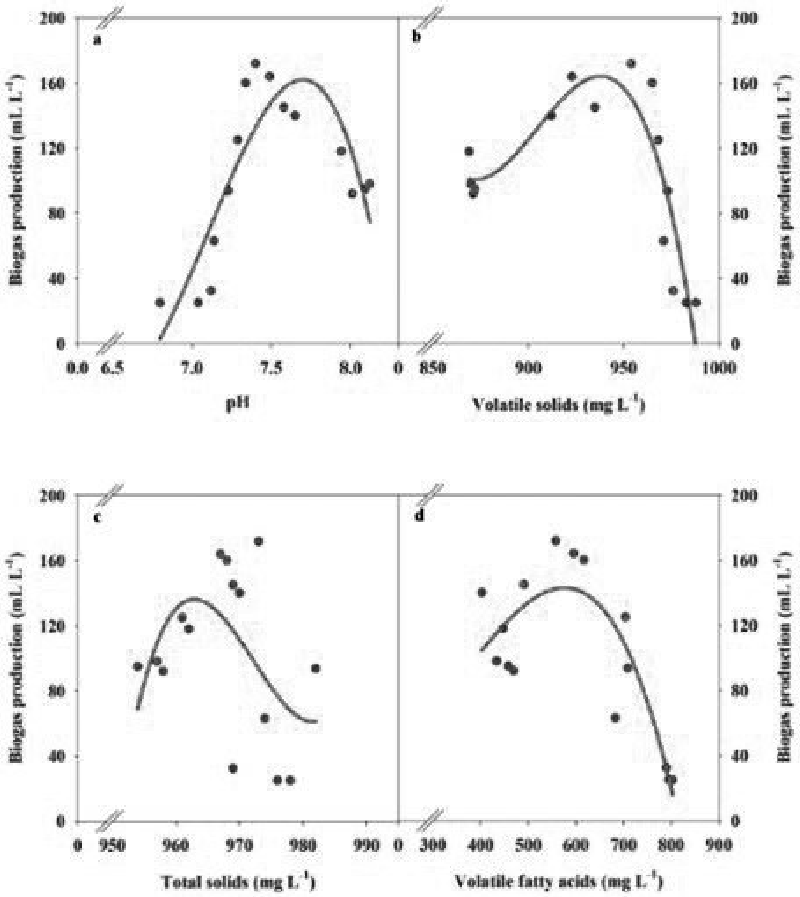

Figure 2. Linear regression analysis of biogas production (a) pH (b) VS (c) Total solids (d) Volatile fatty acids.

Conclusion

Biomass is a versatile and abundant resource, which can be used to produce energy via different routes, including fermentation and anaerobic diges- tion. The above study investigated the major factors influencing the biogas production from the acid pre- treated stillage. It was observed that the accumulat- ed fatty acids were quickly degraded but the biogas production decreased when the reactor pH continued to increase beyond 7.4. Future studies aimed at opti- mizing the reactor parameters need to be conducted to attain maximum conversion of stillage into biogas production by biomethanation.

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