

Effects of Different Temperature on Alkaline Pretreatment of Maize Cob and Biogas Production

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Abstract

This paper appraised the effect of different temperatures on pretreatment of lignocellulosic biomass (maize cob) for use as co-substrate with cow dung and food waste. The method involves pretreatment of milled maize cob with 20% (w/v) NaOH at temperatures of 80, 100, 120 and 140°C. The pretreated maize cob was digested as co-substrates and biogas was estimated using the positive displacement technique. It was found that an increase in biomass pretreatment temperature is generally related to increase in biogas production and the increase is statistically significant. However, pretreatment at 80 or 100°C may likely be viable economically when the energy burden for all treatments is considered. Thus, the application of low temperatures in the range of 80-100°C for pretreatment of maize cob using sodium hydroxide for possible use as co-substrates with cow dung and food waste is appropriate.

Keywords: Temperature, Pretreatment, Lignocellulosic, Biomass, Biogas.

Introduction

Lignocellulosic biomass, comprising cellulose, hemicellulose, and lignin, represents a significant renewable resource for biogas production. Effective pretreatment is necessary to overcome the recalcitrance of this biomass and enhance its digestibility. Alkaline pretreatment, utilizing solutions such as sodium hydroxide (NaOH) or ammonia (NH₃), disrupts the biomass structure to improve cellulose accessibility for microbial digestion. Temperature is a critical parameter in this process, affecting reaction kinetics, lignin removal, cellulose degradation, and ultimately, biogas production. Alkaline pretreatment modifies the structure of lignocellulosic biomass through several mechanisms such as lignin dissolution where alkaline solutions break the ester bonds between lignin and hemicellulose, facilitating the removal of lignin and improving biomass porosity. Through cellulose and hemicellulose disruption, alkaline conditions reduce cellulose crystallinity and disrupt hydrogen bonds, making cellulose more accessible for enzymatic hydrolysis. Another interesting mechanism is the reduction in biomass recalcitrance, where the removal of lignin and disruption of cellulose structure collectively enhance the efficiency of subsequent enzymatic hydrolysis.

Temperature significantly influences various aspects of alkaline pretreatment, including reaction kinetics, lignin removal, and cellulose degradation. Higher temperatures accelerate the alkaline pretreatment process by increasing the rate of chemical reactions. Liu et al. (2017) found that pretreatment temperatures between 40°C and 60°C significantly enhanced the dissolution of lignin and the disruption of cellulose structure. However, temperatures exceeding 80°C can lead to excessive cellulose degradation and reduced effectiveness of the pretreatment (Morrison et al., 2019). The removal of lignin is crucial for improving cellulose accessibility. Studies have shown that moderate temperatures are effective for lignin removal without causing significant damage to cellulose. For instance, Zhang et al. (2020) demonstrated that temperatures between 50°C and 70°C effectively solubilized lignin while preserving cellulose integrity. Conversely, high temperatures can lead to the formation of insoluble lignin-carbohydrate complexes, which can hinder enzymatic hydrolysis (Kumar et al., 2017). Temperature also impacts the degradation of cellulose and hemicellulose. Elevated temperatures may cause excessive degradation of cellulose and partial loss of hemicellulose, negatively affecting biogas yield. Zhang et al. (2018) reported that high temperatures could lead to a reduction in fermentable material, thus reducing biogas production efficiency. Balancing temperature to avoid excessive cellulose degradation while maximizing lignin removal is essential for optimizing biogas production.

The ultimate goal of alkaline pretreatment is to enhance biogas production by improving the digestibility of lignocellulosic biomass. Temperature influences biogas yield and methane production through its effects on pretreatment efficiency. Optimal pretreatment temperatures are critical for maximizing biogas yield. Studies indicate that temperatures in the range of 50°C to 70°C enhance biogas production by improving cellulose accessibility and reducing biomass recalcitrance (Lu et al., 2018). However, temperatures that are too high may lead to decreased biogas yields due to the loss of fermentable substrates and increased energy costs (Lee et al., 2016). Methane is a key component of biogas and a critical indicator of pretreatment effectiveness. Patel et al. (2019) found that moderate temperatures improved methane production by enhancing cellulose digestibility and increasing biogas yields. Excessive temperatures, on the other hand, can reduce methane production due to the degradation of fermentable material and the formation of inhibitory by-products (Jang et al., 2018).

Temperature affects not only the efficiency of alkaline pretreatment but also its operational and economic aspects. Higher temperatures require more energy to maintain, increasing operational costs. Xu et al. (2020) highlighted the importance of optimizing temperature to balance energy consumption with biogas production efficiency. Energy costs must be weighed against potential gains in biogas yield to determine the most cost-effective temperature for pretreatment. Maintaining higher temperatures can affect equipment durability and maintenance. Liu et al. (2019) noted that alkaline solutions at elevated temperatures can be corrosive, leading to increased wear and tear on processing

equipment. Managing these effects is crucial for the long-term sustainability and economic viability of the pretreatment process.

Comparative studies suggest that moderate temperatures (40°C to 60°C) often provide an optimal balance between effective lignin removal and minimal cellulose degradation. Temperatures above this range may result in diminishing returns due to excessive cellulose degradation and increased operational costs (Morrison et al., 2019; Zhang et al., 2020). Each biomass type may have specific temperature requirements, and pretreatment conditions should be tailored accordingly. Temperature is a critical factor in the alkaline pretreatment of lignocellulosic biomass for biogas production. While higher temperatures can accelerate the pretreatment process and enhance lignin removal, they also pose risks of excessive cellulose degradation and increased energy costs. Moderate temperatures generally offer a more balanced approach, improving digestibility while minimizing adverse effects. Future research should focus on optimizing temperature conditions for different biomass types and developing cost-effective methods to manage energy consumption. This will enhance the overall sustainability and efficiency of biogas production from lignocellulosic biomass.

Overall efficiency of biogas production is a function of both yield and production rate. Studies suggest that pretreatment temperatures around 200°C often provide a good balance between increased methane yield and production rate (Wang et al., 2020). However, it is crucial to optimize pretreatment conditions to avoid the adverse effects of high temperatures, such as reduced cellulose digestibility and increased formation of inhibitory by-products (Yang et al., 2018). Cost and energy requirements are critical factors in evaluating pretreatment methods. Thermal pretreatment methods, such as steam explosion and hydrothermal pretreatment, are energy-intensive and costly compared to milder methods like dilute acid or alkaline pretreatment (Luo et al., 2021). The high energy requirements of thermal methods may offset the benefits of increased biogas production if not optimized properly (Huang et al., 2019). The environmental impact of pretreatment methods also varies. Thermal pretreatment methods have a higher carbon footprint due to energy consumption (Cai et al., 2020). In contrast, some chemical pretreatment methods may produce hazardous by-products, which require additional treatment (Bansal et al., 2015). Analysing the environmental impact is essential for sustainable biogas production practices. Therefore, this paper explores the suitability of hybrid approach where alkali pretreatment is evaluated at various temperature regimes to establish a more cost-effective method.

Materials and Methods

Sample collection, preparations and compositional analyses

These procedures were recently published elsewhere (Gidado & Clarkson, 2022). Samples of maize cob was collected randomly from farms after harvest in Bali Local Government Area of Taraba State. The biomass was air-dried in an open space (average temperature of

35±2°C) for three days (8 h per day). The sample size were reduced to about 2 cm in length for effective milling. Size reduction was carried out by a mill and the milled biomass was used for the compositional analysis before and after NaOH pretreatment at temperatures 80, 100, 120 and 140°C.

A portion of the materials was screened into different sizes using a set of sieves and shaker. About 2.5 g of dried raw biomass was loaded into the cellulose thimble. 150 mL of acetone was used as solvent for extraction using Soxhlet Extractor. Residence times for the boiling and rising stages were carefully adjusted to 70°C and 25 min respectively on the heating mantle for a 4h run period. After extraction, the sample was air-dried at room temperature for few minutes. Constant weight of the extracted material was achieved in a convection oven at 105°C. The % (w/w) of the extractives content was evaluated as the difference in weight between the raw extractive-laden biomass and extractive-free biomass.

Exactly, 1 g of extracted dried biomass was transferred into a 250ml flask. 150 ml of 500 mol/m³ NaOH was added. The mixture was boiled for 3.5 h with distilled water and filtered after cooling through vacuum filtration and washed until neutral pH. The residue was dried to a constant weight at 105°C in a convection oven. The difference between the sample weight before and after this treatment is the hemicellulose content (%w/w) of dry biomass. Precisely, 0.3 g of dried extracted raw biomass will be weighed in glass test tubes and 3ml of 72% H₂SO₄ was added. The sample was kept at room temperature for 2 h with careful shaking at 30 minutes intervals to allow for complete hydrolysis. After the initial hydrolysis, 84 ml of distilled water was added. The second step of hydrolysis was made to occur in an autoclave for 1 h at 121°C. The slurry was cooled at room temperature. Hydrolysates was filtered through vacuum using a filtering crucible. The acid insoluble lignin was determined by drying the residues at 105°C and accounting for ash by incinerating the hydrolysed samples at 575°C in a furnace. The cellulose content (%w/w) was determined by the difference.

Preparation of digesters and gas analysis

Inoculum was cultured from fresh cow dung prepared according to the method of Lawal et al. (2015). About 500 g of cow dung was collected from Animal Farm of the Federal Polytechnic Bali and was taken to the laboratory. A sample of 200 g was diluted in distilled water to 10% dry matter and transferred into 2 litre glass bottles. The headspace of the diluted cow dung was flushed with nitrogen gas and closed with a rubber cork and resin. The solution was incubated at 35°C. During the incubation, the solution was degassed by allowing the build-up gas to escape through valve control tube. The completely degassed solution was used as inoculum. Biogas production was quantified using positive displacement technique. Samples (biogas) were analysed using gas chromatography installed with flame ionization detector to determine the quantity of methane contained in the gas. Method adopted by Hossain *et al.* (2022) was followed using column temperature of 250 °C, pressure of 375 kPa, and constant carrier gas flow rate of 20 ml/min, and methane content was expressed as percentage of the gas produced

Pretreatment of the biomass and determination of ash

The lignocellulosic biomass samples were mechanically pulverized until particle size of < 2mm was attained. The milled biomass was pretreated in 6% (w/w) NaOH at 20% (w/v) Solid/Liquid ratio in a tightly capped bottle placed in an autoclave at 80, 100, 120 and 140°C. This procedure is adopted from Gonzales et al. (2016) with modification on the dose and ranges of pretreatment temperature.

An appropriate number of crucibles were marked using porcelain for identification and were placed in muffle furnace at $575 \pm 25^\circ\text{C}$ for a minimum of four hours. The crucibles removed from the furnace and directly placed in desiccator and allowed to cool for one hour. The crucibles are weighed to the nearest 0.1mg. Using an ashing burner and clay triangle with stand, the crucibles were placed over flame until smoke appeared. The smoke was ignited and the samples were allowed to burn until no smoke or flame appearance. The crucible was allowed to cool before being placed in the muffle furnace. In accordance with LAP NREL/TP-510-42622, since an air-dried sample was used, oven-dried weight (ODW) of sample was calculated using the average total solids content as determined by LAP "Standard Method for the Determination of Total Solids in Biomass" (Sluiter *et al.*, 2008). The ash content of sample is computed using Equation 2.

$$ODW = \frac{\text{Weight}_{\text{air dry sample}} - \% \text{Total solids}}{100} \quad 1$$

$$\% \text{Ash} = \frac{\text{Weight}_{\text{crucible plus ash}} - \text{Weight}_{\text{crucible}}}{ODW_{\text{sample}}} \quad 2$$

Determination of total solids in biomass

To determine total solids in biomass sample, the procedure of LAP NREL/TP-510-42621 for the Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid process Samples was followed as presented by Sluiter et al. (2008). Aluminium weighing dishes was pre-dried by placing them in a $105 \pm 3^\circ\text{C}$ drying oven for four hours and the dish was cooled in a desiccator. Using gloves to handle the dish, the pre-dried dish was weighed to the nearest 0.1 mg. The weight of the dish was recorded. Sample was thoroughly mixed and an appropriate amount to the nearest 0.1mg was placed into the weighing dish and the measurement was documented. The sample was placed into a convection oven at $105 \pm 3^\circ\text{C}$ for a minimum of four hours. Sample was removed from the oven and allowed to cool to room temperature in a desiccator. The weight of the dish containing the oven-dried sample to the nearest 0.1 mg was measured and recorded. The oven-dried sample was placed back into a convection oven at $105 \pm 30^\circ\text{C}$ and dry to a constant weight. Constant weight was defined as $\pm 0.1\%$ change in the weight percent solids upon one hour of re-heating the sample (Sluiter et al., 2008). The total solid in biomass sample is computed according to equation 3.

$$\% \text{Total Solids} = \frac{\text{Weight}_{\text{dry pan plus dry sample}} - \text{Weight}_{\text{dry pan}}}{\text{Weight}_{\text{sample as received}}} \times 100 \quad 3$$

Determination of fixed and volatile solids

These are carried out in accordance with the METHOD 1684 EPA-821-R-01-015 of the United State Environmental protection Agency (USEPA). Biomass sample was heated for one hour, and allowed to cool to a balance temperature in a desiccator and weighed. The heating, cooling, desiccating and weighing procedure was repeated until the weight change was less than 4% or 50 mg and the final weight was recorded as W_{total} . The evaporating dish containing the dried sample was transferred to a cool muffle furnace and then heated to 550°C and ignited for 2 hours. The sample was cooled in a desiccator to balance the temperature and the sample was weighed. The process of igniting for 30 minutes, cooling, desiccating and weighing was repeated until the weight change was less than 4% or 50 mg and the final weight was recorded as $W_{volatile}$. Values for fixed and volatile solids were computed according Equations 4 and 5 respectively:

$$\%fixed\ solids = \frac{W_{volatile} - W_{dish}}{W_{total} - W_{dish}} \times 100 \quad 4$$

$$\%volatile\ solids = \frac{W_{total} - W_{volatile}}{W_{total} - W_{dish}} \times 100 \quad 5$$

Results and Discussion

Influence of pretreatment temperature on biomass (maize cob)

One of the purposes of this work is to determine the effects of pretreatment temperature on biomass composition. To achieve this, the biomass has been subjected to 6% NaOH pretreatment under different temperatures. The results obtained from the experiment for pretreatment at different temperatures are shown in Table 1. The application of 6% (w/w) NaOH is argued to be the best dose for biomass pretreatment (Forster-Carneiro & Isaac, 2012; Janke *et al.*, 2016). It was shown that after pretreatment at 100°C, average volatile solids of about 67.44% was obtained which was about 19% higher than that of control experiment. Also, there was substantial depolymerisation of the cellulose-hemicellulose-lignin complexes as across all treatment and these were substantially higher than that of control. Analysis of the ash content suggest that pretreatment at 120°C has exhibited similar behaviour to that of control.

Table 1: Effect of pretreatment temperatures on some chemical properties of maize cob

Parameters	Maize cob pre-treatment				
(%)	T1 (80°C)	T2 (100°C)	T3 (120°C)	T4 (140°C)	Control (36 °C)
Total Solids	94.22±1.12	92.28±1.15	92.22±2.12	90.48±2.16	93.28±1.42
Volatile Solids	61.41±2.55	67.44±2.66	66.01±2.16	63.41±2.55	48.41±2.73
Hemicellulose	25.62 ±0.95	21.87 ±1.95	23.65 ±1.95	21.69 ±0.95	19.73 ±1.09
Cellulose	29.95±1.21	32.75±1.45	29.77±1.28	27.55±1.28	21.08±1.01
Acid Soluble lignin	7.86±0.98	8.71±1.08	7.95±1.05	9.76±2.98	9.86±0.98
Acid Insoluble lignin	6.55±1.53	5.69±1.42	6.38±1.58	7.64±2.02	8.85±0.53
Ash	28.55±3.14	24.52±2.24	31.59±2.14	29.52±2.13	31.09±2.44

Although, evidences from Table 1 indicated that there is substantial deconstruction of the biomass complex structure, it became more obvious that pretreatment of maize cob with NaOH at a temperature of 100°C is likely to be more appropriate. However, whether this attribute may be reflected on the biogas production remained an interesting aspect of this work, and will be evaluated in the subsequent sections of this article.

Effect of temperature on biogas production

The information in Figure 1 is the results of daily biogas production from co-digestion involving maize cob subjected to NaOH pretreatment at various temperature regimes [T1 (80°C), T2 (100°C), T3 (120°C), T4 (140°C)] and Control at a temperature of 36°C. Highest biogas production was observed with the NaOH pretreatment at T4 (140°C). However, the energy demand to achieve that level of temperature may be one of the major setback of this pretreatment. Additionally, looking back Table 1, the depolymerisation of cellulose and hemicellulose is effectively higher in all the treatments compared to control experiments. In other words, pretreatment at all the temperature regimes have substantially depolymerised the biomass constituents. Together, these effects have not translated into equivalent or proportionate improvement in biogas gas production as can be seen in Figure 1. ANOVA analysis revealed that the changes in biomass pretreatment temperatures led to significant ($P < 0.05$) increase in biogas production at 95% level of confidence. Lag phase delays for all treatment were not prominently substantial as biogas production commenced earlier.

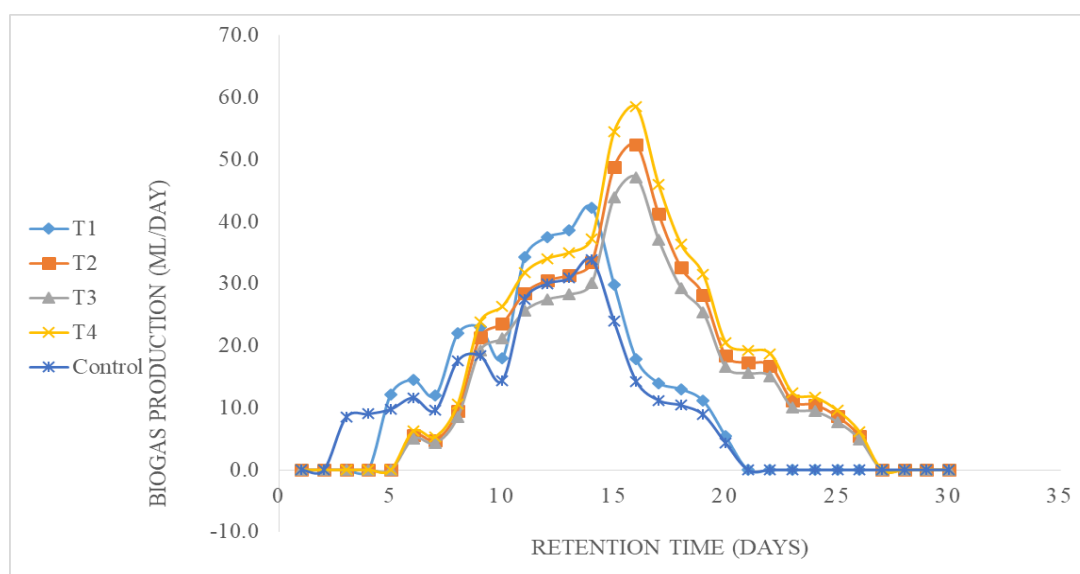


Figure 1: Results of daily biogas production from co-digestion involving maize cob subjected to NaOH pretreatment at various temperature regimes [T1 (80°C), T2 (100°C), T3 (120°C), T4 (140°C)] and Control at 36°C

Influence of biomass pretreatment temperature on cumulative biogas production

The data in Figure 2 is the results of cumulative biogas production from co-digestion of agricultural wastes with particular focus on the differential temperature pretreatment of maize cob as one of the co-substrates. Results showed that highest cumulative biogas of 535.8 ml was attained with pretreatment temperature of T₄ (140°C) followed by T₂ (100°C) with 480.1 ml, T₃ (120°C) with 432.1 ml. These were about 83%, 63.3% and 47% higher than the cumulative biogas obtained from the control digesters. Analysis of variance revealed that the effect of biomass pretreatment temperature on biogas production at 95% confidence level is statistically significant ($P < 0.05$).

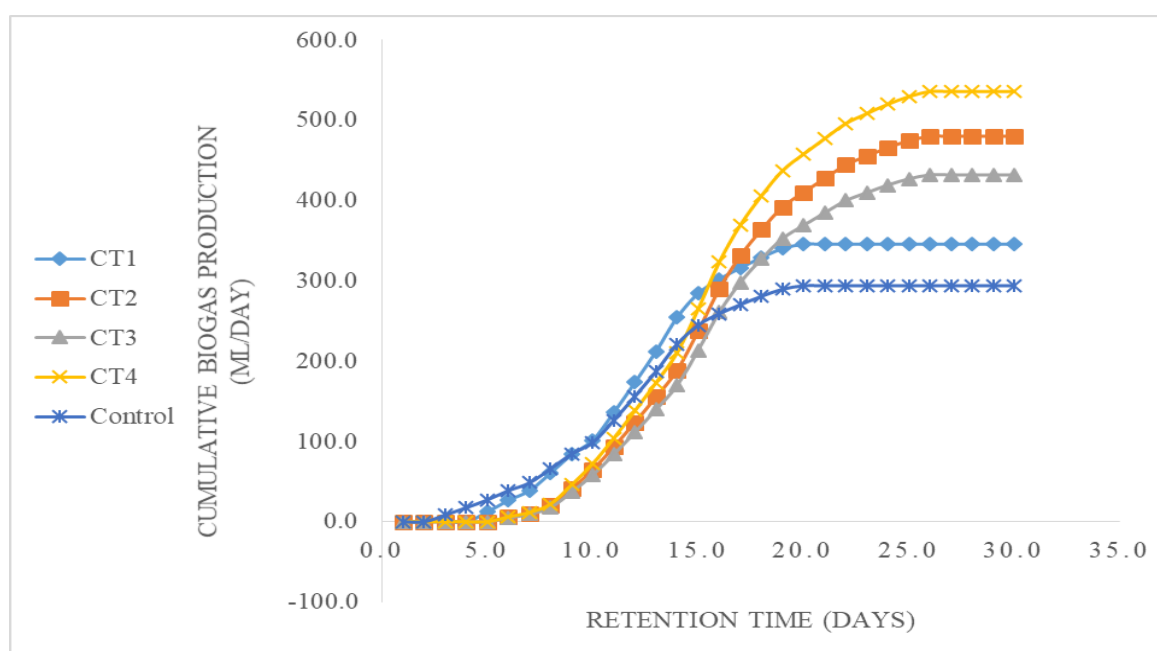


Figure 2: Results of cumulative biogas production from co-digestion involving maize cob subjected to NaOH pretreatment at various temperature regimes [T₁ (80°C), T₂ (100°C), T₃ (120°C), T₄ (140°C)] and Control at 36°C

Conclusion

The purpose of this work is to appraise the effect of different lignocellulosic biomass pretreatment temperature on biogas production. It was found that an increase in biomass pretreatment temperature is generally related to increase in biogas production and the increase is statistically significant. However, pretreatment at 80 or 100°C may likely be viable economically when the energy burden for all treatments is considered.

Recommendation

The use of low temperatures in the range of 80-100°C for pretreatment of maize cob using Sodium Hydroxide for possible use as co-substrates with cow dung and food waste is appropriate.

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