

# **Resource Recovery from Corn Residues through Production of Biogas and Bio-hydrogen**

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## **Abstract**

The potential to produce biogas and bio hydrogen from corn residue was investigated. A sample of 10g initially hydrothermally treated to liberate the cellulose and hemicellulose rich hydrolysate. Three steps for treatment at 80 °C for 15 min; 180 °C for 40 min and 190 °C and 10 min were investigated for corn residue conversion to soluble sugars. The highest cellulose yield was 0.356g per gram of corn residues through fermentation and 0.312g of bio hydrogen per gram of corn residues. An industrial process for the co-generation of biogas and bio-hydrogen from corn stover was then proposed from the experimental work.

**Keywords:** Bio-hydrogen; Biogas; Biofuel; Biomass; Corn stover; Fermentation; Lignocellulose

## **1. Introduction**

The demand of hydrogen and biogas as a source of energy is increasing daily and this has led to various studies on their generation from lignocellulosic material like waste corn stover (Kaparaju et al., 2009; Mtui, 2009; Bensha and Mensah, 2013). Considering the issue of waste management into bioenergy necessitated this study whereby a process that produces bio-hydrogen and biogas from corn stover was designed through the identification of optimal operating conditions (Mussatto and Teixeira, 2010; Toscana et al., 2013; Singh et al., 2015). Bio energy is any energy derived from biomass and potential products include biogas, bio briquettes, bio hydrogen and biogas.

## **2. Experimental**

## 2.1 Materials

All reagents and chemicals were obtained from Sunfirm Distributors, Harare, Zimbabwe. An oven, corn stover, Erlenmeyer flasks (250-mL), hydrochloric acid (HCl), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), formic acids (HCOOH), autoclave, filter paper, 3,5-dinitrosalicylic acid assay (DNS) test apparatus, sodium hydroxide (NaOH), potassium hydroxide (KOH), hydrogen peroxide, distilled water, an electronic balance, a pH meter, potassium tartarate (Rochelle salt), Shimadzu spectrophotometer (UV 1800, Sigma Aldrich, Johannesburg, South Africa), yeast/bacteria/fungi, and potassium dichromate were used. A gas syringe (Lab Equipment Express, Johannesburg, South Africa) was used for biogas collection. The corn residue was obtained from nearby maize fields in Harare, Zimbabwe and the yeast was cultured in the lab. The average characteristics of the corn residue are given in Table 1.

Table 1. Characteristics of the corn residue (Kumar et al., 2009)

Component	Composition (%)
Cellulose	45
Hemicellulose	35
Lignin	15

## 2.2 Methods

### 2.2.1 Determination of the best acidic pretreatment agent between HCl, H<sub>2</sub>SO<sub>4</sub>, and HCOOH

Three 5 g samples of the dried and crushed corn residue were placed into three Erlenmeyer flasks. The three acids (HCl, H<sub>2</sub>SO<sub>4</sub>, and HCOOH) were added into each of the Erlenmeyer flasks. The mixtures were autoclaved at 200 °C for 15 min, allowed to cool to room temperature, and then filtered with the hydrolysate using filter paper to remove the unhydrolysed material. The filtrate was collected for a reducing sugar content analysis using a DNS test. For the DNS test, 3 mL of 3, 5 dinitrosalicylic acid (DNSA) reagent were added to 3 mL of the hydrolysed sample in a test tube then heated to 90 °C for 10 min to develop the reddish brown colour. Then, 1 mL of 40% Potassium tartrate (Rochelle salt) solution was added to stabilize the colour. After cooling to room temperature in a cold-water bath, the absorbance of the solutions was obtained using a spectrophotometer (Model CM-5, Konica, and Minolta, Japan) at 575 nm.

### 2.2.2 Determination of conversion and yield of bio-hydrogen

A 100 g sample of corn residue was pre-treated with 350 mL of water at 180 °C. The liquid substance (hemicellulose) of the sample was then separated from the solid substance (cellulose) and the hemicellulose was used for the process. The material was allowed to cool to room temperature then it was poured into a soda bottle to go through a dark fermentation after the addition of bacteria (*Clostridium Thermocellum*). The top of the bottle was secured with an uninflated balloon then monitored on a daily basis for a period of one week. The same procedure was repeated, altering the temperature and the amount of corn stover, and recorded.

### 2.2.3 Determination of conversion and yield of biogas

A 100 g sample of corn residue was pretreated with 350 mL of water at 180 °C. The liquid substance (hemicellulose) of the sample was then separated from the solid substance (cellulose) and the cellulose was used for the process. The material was allowed to cool to room temperature then poured into a soda bottle to go through a dark fermentation after the addition of 5 g of yeast (*Saccharomyces cerevisiae*). The top of the bottle was secured with an uninflated balloon then monitored on a daily basis for a period of one week. The same procedure was repeated, altering the temperature and the amount of corn residue, and recorded. The glucose standards of the concentrations were analyzed using spectrophotometry.

## 3. RESULTS AND DISCUSSION

### 3.1 Best Acidic Pretreatment Agent between HCl, H<sub>2</sub>SO<sub>4</sub>, and HCOOH

The H<sub>2</sub>SO<sub>4</sub> was found to be the best pretreatment agent during the dark fermentation of corn residue. An absorbance of 0.4 at 575 nm was achieved (Table 2). The acid treatment promotes economic and environmental sustainability, which promotes high yields of biofuels from corn residue (Bensha and Mensah, 2013).

Table 2. Absorbance of samples exposed to acid hydrolysis

Acid	Absorbance at 575 nm
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2% H <sub>2</sub> SO <sub>4</sub>	0.400
2% HCl	0.321
3% HCOOH	0.107

The effectiveness of H<sub>2</sub>SO<sub>4</sub> as the pretreatment acid was further shown by the glucose concentration in each sample (Table 3), with the highest amount of glucose being obtained in 2% H<sub>2</sub>SO<sub>4</sub>. Acid hydrolysis using H<sub>2</sub>SO<sub>4</sub> achieved near theoretical sugar concentrations and fewer degradation products (Stoker et al., 2012; Bondesso et al., 2013).

Table 3. Glucose concentrations achieved for various acids

Acid	Glucose concentration (mg/mL)
2% H <sub>2</sub> SO <sub>4</sub>	190
2% HCl	150
3% HCOOH	50

### 3.2 Determination of Bio-hydrogen Yield

As shown in Table 4, more bio-hydrogen was collected after adding more heat to the 100 g of the stover. More hydrogen was collected from the container that had 100 g of corn residue and a temperature of 180 °C, which was the reason for these conditions to be applied in the process design. Higher temperatures of 190 °C resulted in lower bio-hydrogen yields because harsh conditions tend to produce inhibitory compounds affecting the yield (Toscana et al., 2013).

Table 4. Results on bio-hydrogen yield

Corn Residue (g)	Temperature (°C)			
100	180	43.0	45.6	46.8
100	150	30.4	33.0	34.2
150	180	18.5	24.7	29.1
50	190	27.8	29.3	31.6

### 3.3 Determination of Biogas Yield

The percentages of biogas were calculated with reference to the amount of cellulose produced from the raw materials (Table 5). It was observed that the highest corn residuemass gave a higher biogas percentage (70.7%) because the pretreatment gave a better quality of cellulose at 180 °C, which could give more biogas after being digested over a short period of time. Bondesson *et al.* (2013) also reported that high yields of biogas were obtained in an acid treated corn stover in comparison to a system without an acid treatment.

Table 5. Results on biogas yield

Corn Residue (g)	Temperature (°C)			
100	180	44.5	49.0	51.7
100	150	31.3	36.1	37.3
150	180	47.2	60.5	70.7
50	190	9.6	11.7	12.8

## 4. Industrial Process Design

This section utilized the results obtained in the experiments to come up with design assumptions with a block flow diagram showing all major pieces of equipment.

The process was broken down into three sections: the pretreatment stage, the bio-hydrogen step production, and the biogas step production.

#### *Pretreatment*

The corn residue went through a size reduction process where it was cut to smaller pieces and went through a ball milling for further size reduction and for easy access for enzyme and bacteria activities. The material then went through a three stage hydrothermal pretreatment, the first step was a soaking step that was operated at temperature of 80 °C and residence time approximately 15 min. Step two required heating up the corn stover to approximately 180 °C for 40 min, followed by heating at 190 °C for 10 min in a third stage. In this case, the

hydrolysate was the main focus for bio-hydrogen production and cellulose was the main focus for the biogas production. A centrifugation technique was applied for the separation of the hydrolysate and the cellulose.

#### *Bio-hydrogen production*

The hydrolysate was then fed into a fermenter where it went through dark fermentation whereby the organic substrate was converted to bio -hydrogen after bacteria (*Clostridium Thermocellum*) was added. The temperature was maintained below 60 °C for the bacteria to not be affected and for dark fermentation to work effectively. The gas was then collected using a gas syringe. The effluent was then added into the bio-digester for more biogas production.

#### *Biogas production*

For the biogas production, there were two streams that were fed into the bio-digester. The main stream contained the cellulose that was hydrolyzed using sodium bicarbonate then went through fermentation, and was then later fed into the bio-digester where the bacteria (methanogens) was added for the production of biogas. The other stream that was fed into the bio-digester was from the bio-hydrogen effluent stream. The gas was then collected using the gas syringe equipment. The effluent from the bio-digester was de-watered then burnt or used as fertilizer. The water was then chlorinated for treatment to be recycled back into the system or disposed of into main streams.

## **4. Conclusion**

Lignocellulosic biomass, such as corn stover, can be used as a raw material for bio-hydrogen and biogas. Enzymatic hydrolysis and subsequent fermentation of cellulose should yield biogas, while the dark fermentation of hydrolysate to produce bio-hydrogen from sugars. Temperatures of around 180 °C results in biogas yield of 70% and bio-hydrogen yield of 47%

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