

# Bioethanol Production from Corn Residue

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## Abstract

Currently, many developing countries are facing fuel challenges while corn stover waste remains unutilized. This study utilized excess corn Stover to make bioethanol a value added product by designing a plant that manufactures 150 tons per day of 99.5% pure cellulosic bioethanol operating over a 10-year period. The process that converted crude corn Stover to cellulosic bioethanol was evaluated for conversion *via* hydrolysis of lignocelluloses in the corn Stover then the cofermentation of the Carbon 5 and Carbon 6 monosaccharides obtained from the hydrolysis process. The hydrolysis process is a route to the bioethanol through 86% co-fermentation of Carbon 5 and Carbon 6 sugars obtained from the 75% saccharification of corn Stover to fermentable sugars to produce 99.5% pure cellulosic bioethanol that can be used to blend petrol. The economic analyses indicated a payback period of 1.5 years, a rate of return on investment of 86%, and a selling price of \$1.10/liter for the bioethanol that indicated the feasibility of the project. Waste corn Stover to bioethanol technology can be applied as a waste management tool to meet energy demands in agro-based industries.

**Keywords**-Bioethanol; Biofuels; Corn Stover; Economic assessment

## 1. Introduction

The intensive use of fuels for vehicles obtained from non-renewable natural oil is exposing a threat of oil depletion and climate change (Luo et al., 2009; Kazi et al., 2010). In contrast, the destruction of maize plant wastes, known as corn Stover, by burning causes undesirable effects such as air pollution, depletion of the ozone layer, global warming, the greenhouse effect, and the formation of acidic rain (Sheehan et al., 2004; Klein-Marcuschamer et al., 2011). Increasing the use of biofuels for energy generation purposes is of particular interest nowadays because it can decrease the dependence on foreign oil, reduce trade deficits, provide means of energy independence, and potentially offer new employment possibilities (Sheehan et al., 2004). Biofuels are being investigated as possible substitutes for current high pollutant fuels obtained from conventional sources making waste corn Stover attractive (Varga et al., 2004; Ranum et al., 2014). Using lignocellulose materials, such as waste maize corn Stover, in bioethanol production has an advantage over using sugar and starch because it minimizes the conflict between using land for food production or for energy feedstock production. Zimbabwe is an agro-based economy with an annual maize production rate of roughly 1,000 metric tons per annum (Table 1), which would benefit immensely from the beneficiation of waste maize corn Stover to bioethanol. This availability of corn Stover showed the need for the technoeconomic feasibility of a plant that produces 150 tons per day of cellulosic-based bioethanol from corn Stover, assuming that approximately a third of the annual production is maize corn Stover.

Table 1. The annual maize production in Zimbabwe for the past five years in metric tons (Klein-Marcuschamer et al., 2011)

Production Year	Production (Metric tons)
2009	650
2010	1000
2011	1450
2012	965
2013	900

## 2. Experimental

### 2.1 Materials

The corn Stover used in this work was obtained from a plot in Chegutu, Zimbabwe. The following reagents and chemicals were used in the study: Distilled water (pH 7), 0.4 M of sulphuric acid ( $H_2SO_4$ ), 8.0 M of sodium hydroxide (NaOH), *Escherichia coli* (*E. Coli*), weighing balance, incubator, stirring rod, incubator, pH meter, thermometer, conical flasks, beaker hydrometer inoculating loop, and burner were used. All chemicals and reagents were obtained from Sunfirm Distributors in Harare, Zimbabwe. A 64825 Sigma Aldrich IL Soxhlet Apparatus (Johannesburg, South Africa) was used for fermentable sugars extraction.

### 2.2 Methods

#### 2.2.1 Determination of fermentable sugars yield

The corn Stover was first washed and dried. Afterwards, 150 g of shredded corn Stover was divided into three parts and 250 mL of dilute  $H_2SO_4$  solution was poured in the conical flask of the Soxhlet unit. Sample A was placed in thimbles and put in the top limb of the Soxhlet unit. The Soxhlet unit was switched on at level 3 and ran for 8 h. The fermentable sugar sample was collected and weighed. The procedure was repeated for all samples. The pH of the obtained samples was measured and a drop of concentrated NaOH solution was added until a pH of approximately 4.5 was reached. The solution obtained was sieved to remove the sodium sulphate produced.

#### 2.2.2 Determination of the amount of bioethanol yield

The culturing of the bacteria was performed 48 h before commencing the experiment. Then, 10 g of potato dextrose agar was completely dissolved in 250 mL of water in a conical flask. The mixture was covered with cotton wool and foil paper and then sterilized in an autoclave at 121 °C for 5 min. Upon removal, it was cooled, poured into petri dishes, and set aside to solidify. The *E. Coli* was then introduced into the petri

dishes with the aid of a sterilized inoculating loop. The petri dishes were then sealed and kept in an incubator for 48 h at a temperature of 25 °C.

### 2.2.3 The co-fermentation of C5 and C6 sugars

The three process solutions obtained from the experiment that hydrolyzed corn Stover were heated to 30 °C and 3 drops from the sterilized inoculating loop of cultured *E. coli* were added to the three flasks. All of the flasks that contained the samples were clogged with cotton wool to hinder aerobic conditions. The three samples were put in the incubator and were maintained at 30 °C for 36 h to allow complete fermentation. Every 4 h the mixtures were tested for their sugar contents using a hydrometer. A sample with 100 mL of the co-fermented sugars was distilled in a distillation bath. The solution obtained after 36 h was filtered to remove the froth and scum. The froth that formed at the upper layer and the remaining broth was placed in a water bath to inhibit the enzyme activity.

After every 4 h of fermentation duration the hydrometer was dipped in the fermentation liquor to determine the rate of degradation of the fermentable sugars. This determined the rate of accumulation of bioethanol and the reaction time for co-fermentation.

A few drops of cooking oil were added to a dry test tube with 2 cm<sup>3</sup> of bioethanol and the test tube was shaken thoroughly. Then, 2 cm<sup>3</sup> of deionized water was added to the solution and observations were noted by the experimenter.

## 3. Results and Discussion

### 3.1 Characterization of the Corn Stover

The characterization of the waste corn Stover used in this study is shown in Table 2. A lignin value of 20.1 was achieved and was ideal for bioethanol production.

Table 2. Characterization of the corn residue

Component	Composition (%)
Glucan	38.6
Xylan	23.5
Arabinan	2.4
Mannan	3.1
Galactan	2.7
Lignin	20.1
Ash	4.2
Acetate	2.8
Protein	3.1

### 3.2 Analysis of the hydrolysis and fermentation of corn Stover to bioethanol

A yield of 76.8% conversion was attained after hydrolyzing the corn Stover. The amount of bioethanol yielded in fermentation also involve a test of the sugar concentration every 4 h. The sugar concentration decreased as the bioethanol formed increased in quantity. However, an optimum yield of 86% for the bioethanol production was achieved. The bioethanol-oil mixture emulsified when droplets of distilled water were added, which showed that bioethanol was present in the fermented samples. The characteristics of the bioethanol produced in this work are shown in Table 3.

Table 3. Properties of cellulosic bioethanol

Physicochemical Parameter	Value
Boiling Point	78.3 °C
Melting Point	117.3 °C
Refractive Index	1.37
Surface Tension	22.3 dyne /cm
Vapor Pressure	43 mm Hg at 20 °C
Specific Heat Capacity	0.618 cal/g K

Flash Point	12.7 °C
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The fermentation produced bioethanol with an alcohol content of 12% that was slightly lower and this was attributed to the low mixing during fermentation. The experimental results showed that it was feasible to extract cellulosic bioethanol from the local corn Stover. Therefore, it is possible to setup a manufacturing plant that extracts cellulosic bioethanol from corn Stover. The 76.8% conversion of the corn Stover to fermentable sugars and 86% conversion of the fermentable sugars to cellulosic bioethanol determined from the experiments conducted in the laboratory were used for the mass balances.

## 4. Bioethanol Production Process Design

### 4.1 Process Description of Making Cellulosic Bioethanol from Corn Stover by the Cellulolysis Method

The corn Stover from the fields in Chegutu, Zimbabwe was cleaned with water to remove any loose dirt. Afterwards, the corn Stover was dried and shredded for particle reduction. The washed and shredded corn Stover was fed by a conveyor belt to the pre-steamer where low pressure steam at 163 °C and 4.46 bar was added to maintain a temperature of approximately 100 °C. The pre-steamed corn Stover was conveyed into the hydrolyzing reactor. The reactor temperature, pressure, and residence time was maintained at 190 °C, 11.6 bar, and 2 min, respectively. The corn Stover slurry was then flashed to 1.0 bar in the blow down tank. The solid fraction was separated from the slurry in a pneumatic pressure filter. To reduce the toxicity to the fermentation organisms and downstream processing costs, a limiting step of lime was added to neutralize the excess H<sub>2</sub>SO<sub>4</sub> in the hydrolyzate. The reaction between lime and H<sub>2</sub>SO<sub>4</sub> that forms gypsum was separated from the hydrolyzate as a solid cake. The corn Stover remains were dried and used as a fuel to heat the boiler. The enzyme *Zymomonas mobilis*, which was used in the anaerobic fermentation to produce cellulosic bioethanol, was genetically modified bacteria. Therefore, they were provided with the necessary conditions in the bioreactor so that they could multiply and produce a large strain of bacteria. The pentose (xylose and arabinose) and hexose (glucose, mannose, and galactose) sugars obtained from the hydrolysis were mixed with the bacteria *Zymomonas mobilis* at 30 °C for 36 h in a semi-batch reactor. The fermentation process alone did not produce a bioethanol solution with an alcohol content greater than 15%. Distillation is the separation technique that was used to concentrate the bioethanol solution from 12% to 95% bioethanol content based on the different boiling points of bioethanol and water. The 95% hydrous bioethanol obtained was an azeotrope. To obtain a 99.5% pure bioethanol solution, molecular sieves were used to dehydrate the azeotropic solution. The bioethanol's molecules were small enough to pass into the pores of the molecular sieves allowing for dehydration of the bioethanol. In the first stage, the hydrous alcohol was pre-heated, vaporized, and superheated before being admitted to the vessels that contained the molecular sieve material. In this superheated, vapor phase at a controlled temperature and pressure, the adsorption of the water molecules by the sieve was optimized, while the alcohol molecules passed through. For this to be achieved, the molecular sieves with pores of approximately a diameter of 3 mm were used. Water molecules of diameter 2.8 mm entered the pores while the bioethanol molecules could not and the separation of the molecules occurred. The wastewater generated was sent to the wastewater treatment plant while the bioethanol was stored in a storage tank before it was sold to the customer.

### 4.2 Material Balances

The mass balances were used as the basis for calculating the plant equipment design parameters as well as the economic evaluation. The objective was to produce 150 tons of bioethanol per day. Assuming a 24 hour working day, 6.25 tons/h of bioethanol was produced. The mass balance determined the feed and the components for each stream. Table 4 shows the summary of the mass balance calculations performed on all of the equipment involved in the manufacture of cellulosic bioethanol from corn stover.

Table 4. Summary of the process mass balances in tons/h

Equipment	Chemical Species	Mass In	Mass Out
Shredder	Corn Stover	78.45	78.45
Pre-steamer	Corn Stover	78.45	78.45
	Steam	5.00	4.50

Hydrolyzer	Corn Stover	78.45	18.19
	Water	10.00	10.00
	H <sub>2</sub> SO <sub>4</sub>	0.20	-
	Fermentable Sugars	-	60.26
	Lime	0.12	-
	Gypsum	-	0.28
Co-fermenter	Fermentable Sugars	60.26	8.44
	Bacteria	0.10	0.10
	Bioethanol From Fermentation	-	51.82
	Carbon Dioxide	-	30.00
Distillation Column	Bioethanol From Fermentation	51.82	-
	Water	-	45.51
	Hydrous Bioethanol	-	6.31
Dehydrating Vessel	Anhydrous Bioethanol	-	6.25
	Water	-	0.06
	Hydrous Bioethanol	6.31	-

### 4.3 Energy Balances

Bioethanol production is an energy intensive process which involves multiple steps. Table 5 is a summary of the 4 energy changing steps that occurred on the specified plant equipment. The energy balances are over the preheater, hydrolyzer, co-fermenter, and the distillation column.

Table 5. Summary of the energy changes for the bioethanol producing plant

Equipment	Energy Changes (Kj/h)
Pre-heater	$1.57 \times 10^2$
Hydrolyzer	$5.06 \times 10^2$
Co-fermenter	$-1.42 \times 10^4$
Distillation Column	$2.87 \times 10^4$

## 5. Economic Analyses

The experimental financial appraisal, done at the preliminary stage of this study, showed that it is beneficial to invest in the project of making 150 tons per day of cellulosic bioethanol from corn stover. However, because this is a promising big project, it required a formal financial appraisal. The formal financial appraisal covered the calculations of the following financial parameters: Return on investment, payback period, internal rate of return (IRR), net present value (NPV), and breakeven point.

This assessment demonstrated the economic and financial viability of the conversion of bioethanol from corn stover with regard to fixed capital investment. To achieve this, the ratio and factors for estimating capital investment items based on delivered equipment from Peters and Timmerhaus (1980) were used. The values presented are applicable for major process plant additions to an existing site where the necessary land is available through present ownership.

### 5.1 Fixed capital investment

This is the total cost required for starting a plant and is referred to as FCI. The FCI is a once off cost and is not recovered at the end of the project.

### 5.2 Equipment costing

The sixth tenths rule was used to estimate equipment cost, and cost indices were also used to approximate the cost of the equipment needed to install the plant today. Table 6 indicates the bill of quantities for installation of the corn stover to bioethanol plant.

Table 6. Bill of quantities for the bioethanol from corn residue plant

Component	Quantity	Unit Price (\$)	Total Cost (\$)
Distillation Column	2	25,000	50,000
Semi-batch Co-fermenter	1	20,000	20,000
Boiler	1	40,000	40,000

Cooling Tower	1	20,000	20,000
Positive Displacement Pumps	6	350	2,100
Centrifugal Pump	7	500	3,500
Bioethanol Storage Tank	1	2,000	2,000
Conveyer Belts	3	300	900
Seed Fermenter	3	5,000	5,000
Pre-steamer	1	3,000	3,000
Hydrolyzer	1	8,000	8,000
Condenser	1	1,500	1,500
Dehydrating Vessel	1	5,265	5,265
Re-boiler	1	1,500	1,500
Diaphragm Valves	11	30	330
Gate Valves	4	35	140
Safety Relief Valves	3	45	135
Stainless Steel Pipe 15 mm Diameter	19m	210/m	3,990
Cast Iron Pipe 15 mm Diameter	10m	60/m	600
Carbon Steel Pipe 10 mm Diameter	50.5m	40/m	2,020
M12 × 30 mm Bolts	800	0.81	648
M16 × 50 mm Bolts	640	0.44	284
Pipe Flanges	160	5.60	896
I-Beam Support Mild Steel	20	240	4,800
Angle Iron Support	15	180	2,700
Flat Bar Support	10	19.20	192
Total Cost			184,500

### 5.3 Cost estimation of direct costs

The cost estimation for the project was done using the Factorial Method (Sinnot, 2009). The project fixed cost is often defined as a function of the total equipment purchase price as indicated by Equation 1.

$$C_f = F_t C_e \quad (1)$$

Where  $C_f$  is the cost for fixed capital,  $F_t$  is the Lang Factor  $C_e$  is the total cost of all delivered equipment. For this project, 4.7 was the Lang factor used. Therefore, the total fixed cost was \$867,150.00.

### 5.4 Indirect costs

The indirect costs are expenses that are not directly involved with the material and labor of the actual complete facility installation and they range from 15% to 30% of the fixed capital investment. However, the calculations are based on the direct costs as indicated in Table 7. The fixed capital investment, which is the sum of the direct costs (\$867,150) and indirect costs (\$260,145) totaled \$1,127,295.00 for this study.

Table 7. Indirect costs

Economic Parameter	Typical DC Range (%)	Chosen DC (%)	Cost (\$)
Engineering and Supervision	5 to 30 DC	15	130,072.50
Construction and Contractor's Fees	6 to 30 DC	10	86,715
Contingency	5 to 15 DC	5	43,357.50
Total Indirect Costs			260,145

### 5.4 Working capital

The working capital for this project was 20% of the total capital investment (TCI), which totaled \$1,409,118.75.

### 5.5 Estimation of total production costs

Total production costs (TPC) are the sum of direct and indirect production costs, fixed charges, and plant overhead costs. Depreciation depends on the lifetime of the plant. The salvage value and the method of calculation is approximately 10% of the fixed capital investment for machinery and equipment. The estimation of the total production cost as evaluated from the TCI and FCI amounted to \$298,733.19, as indicated in Table 8.

Table 8. Estimation of total production costs

Economic Parameter	Typical TCI / FCI Range (%)	Chosen TCI / FCI (%)	Cost (\$)
Fixed Charges	10 to 20 TCI	10	140,911.88
Depreciation for Machinery	10 FCI	10	112,729.50
Depreciation for Machinery	2 to 3 TCI	2	28,182.38
Local Taxes	1 to 4 FCI	1	11,272.95
Insurance	0.4 to 1 FCI	0.5	5,636.48
Total TPC			298,733.19

### 5.6 Plant overhead cost

Plant overhead costs are costs within a plant that are not directly attributed to any one production or processing unit and are allocated on some arbitrary basis believed to be equitable. Plant overhead costs include plant management salaries, the payroll department, local purchasing, and the accounting department. The plant overhead cost of this project was 10% of the total production cost and amounted to \$29,873.32.

### 5.7 Plant utilities

The plant utilities include electricity, steam, oxygen, and process water. The total plant utilities costs were \$29,873.32, as indicated in Table 9.

Table 9. Annual plant utilities cost

Utility	Quantity Required/Year	Unit Price (\$)	Total Cost (\$)
Electricity	1.5163 x 10 <sup>4</sup> kWh	0.01/Kw	14,000.00
Steam	60,000 m <sup>3</sup>	0.10/m <sup>3</sup>	6,000.00
Oxygen (Compressed Air)	400 m <sup>3</sup>	10/m <sup>3</sup>	4,000.00
Process Water	108,000 m <sup>3</sup>	0.09 m <sup>3</sup>	9,873.32
Total Annual Plant Utilities Cost			29,873.32

In addition, the raw materials required for bioethanol production from corn stover required a total cost of \$2,914,600.00 per annum, as indicated in Table 10.

Table 10. Raw materials estimation cost for a year

Material	Unit Cost (\$)	Quantity /Annum	Cost (\$)
<i>Zymnonas mobilis</i>	\$100/ton	720 tons	72,000.00
H <sub>2</sub> SO <sub>4</sub>	\$10/ton	1,440 tons	14,400.00
Corn Stover	\$5/ton	564,840 tons	2,824,200.00
Lime	80/ton	50 tons	4,000.00
Total Raw Materials Estimation Cost			2,914,600.00

The total plant operating costs amounted to \$3,858,735.97, as indicated in Table 11.

Table 11. Plant operating costs

Economic Parameter	Typical TPC / POC Range (%)	TPC / POC Chosen (%)	Cost (\$)
Raw Materials	1 to 10 TPC	-	2,914,600
Direct Supervisory And Clerical	10 to 25 TPC	10	29,873.32
Operation Labor Cost	10 to 20 TPC	10	29,873.32
Utilities	10 to 20 TPC	10	29,873.32
Maintenance And Repairs	2 to 10 FCI	3	33,818.85
Operating Supplies	1 to 2 POC	3	879.18
Laboratory Charges	15 to 25 POC	25	7,143.32
Patent And Royalties	0 to 6 TPC	2	5,974.66
Total Operating Costs			3,858,735.97

### 5.8 Total manufacturing costs

The total cost of manufacturing a product includes the direct labor costs, direct material costs, overhead costs, and any other expenses associated with production. The total manufacturing cost of this project included the operational cost, total capital investment, and plant overhead cost previously mentioned, which amounted to \$5,297,728.04.

## 5.9 General expenses

General expenses are the sum of administrative costs, distribution costs, selling costs, and research and development costs. The distribution and selling costs include the cost for sales offices, salesmen, shipping, and advertising. The total general expenses for the bioethanol to corn stover amounted to \$62,733.98, as indicated in Table 12.

Table 12. General expenses

Economic Parameter	Range (%)	Chosen	Cost (\$)
Administrative Costs	2 to 6 PC	2	5,974.66
Distribution and Selling Costs	12 to 20 PC	12	35,848.00
Research and Development	5 PC	5	14,936.66
Financing (Interest)	0 to 10 TCI*	2	56,974.66
Total General Expenses			62,733.98

\*Total capital investment

## 5.10 Total product cost

The total product cost is the sum of all manufacturing costs, the total general expenses, and the cost of utilities. For this project, the total amounted to \$40,360,462.02.

## 5.11 Gross earnings

The market selling price of bioethanol was \$1.10 per liter. The market selling price of carbon dioxide (CO<sub>2</sub>) was \$20 per ton. The total income of this project was calculated through a summation of the selling price and a summary of the gross earnings is shown in Table 13.

Table 13. Summary of gross earnings

Variable	Value (USD)
Market selling cellulosic bioethanol/L	1.10
Market selling price of CO <sub>2</sub> /ton	20.00
Market selling price of corn stover residue/ton	5.00
Total income	56,644,200.00
Gross income	16,283,737.98
Taxes	4,070,934.50
Net profit	12,212,803.48
Rate of return on investment (%)	86.7%

## 5.12 Payback period

The payback period is the time required for the cumulative net cash flow taken from the startup of the plant to equal the fixed capital investment.

### Assumptions

The calculations for this project used the assumption that there was a constant cash flow, as well as a constant inflation rate. A payback period of 1.15 years was determined using Eq. 1,

$$\text{Payback Period} = \frac{\text{Total Capital Investment}}{\text{Net profit per year}} \dots (1)$$

Where the total capital investment for this project was \$14,091,187.50 and the net profit per year was \$12,212,803.48.

## 5.13 Net present value

A plant lifetime of 10 years was considered due to the change in technology in the processing plants.

Table 14. Net Present Value Calculation

Year	Calculation	Net Present Value (USD)
1	$-3234580 \times (1 + 0.1)^{-1}$	2940527.27
2	$-0 \times (1 + 0.1)^{-2}$	0
3	$540000 \times (1 + 0.1)^{-3}$	405710.00
4	$1620000 \times (1 + 0.1)^{-4}$	1106482.00
5	$2700000 \times (1 + 0.1)^{-5}$	1676487.57
6	$3780000 \times (1 + 0.1)^{-6}$	2133711.46
7	$4860000 \times (1 + 0.1)^{-7}$	2493948.46



8	$5940000 \times (1 + 0.1)^8$	2771053.84
9	$7020000 \times (1 + 0.1)^9$	2977165.28
10	$8100000 \times (1 + 0.1)^{10}$	3122900.64

The NPV for this project was \$13,746,931.76, since the net present value is positive it means that the present value of cash inflows is greater than the present value of cash outflows, thus the investment proposal is acceptable.

### 5.14 Rate of return

The rate of return refers to the annual income from an investment expressed as a proportion (usually a percentage) of the original investment, shown in Eq. 2,

$$\text{Rate of return} = \frac{\text{Cumulative net cash flow at the end of project}}{\text{Life of project} \times \text{Original investment}} \dots \dots (2)$$

and the internal rate of return (IRR) was calculated by Eq. 3,

$$\text{Internal rate of return (IRR)} = \frac{(\text{Cash flow} - \text{Initial cost})}{\text{Initial cost}} \dots \dots \dots (3)$$

Where the cash flow was \$1,346,931 and the initial cost was \$10,975,717.72. The IRR of this project was 25.2%, which is a value greater than the cost of capital (discount rate of 10%). Therefore, the decision is to go ahead with the project.

### 5.15 Breakeven analysis

The breakeven point is the point at which the income from sale of a product or service equals the invested costs, resulting in neither profit nor loss. It is the stage at which income equals expenditure, shown in Eq. 4,

$$\text{Breakeven point} = \frac{\text{Total fixed costs}}{\text{Contribution margin}} \dots \dots \dots (4)$$

Where the contribution margin is the selling price minus the variable costs. Based on this, the contribution margin for this project was 15,000 tons.

## 6. Conclusion

The production of 150 tons per day of cellulosic bioethanol from corn stover is technically and economically feasible as a waste management technology while meeting energy needs. The designed plant will be innovative because it optimizes the process by allowing the co-fermentation of C5 and C6 sugars to obtain a substantial yield of cellulosic bioethanol from corn stover selling at \$1.1/L.

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