

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231271796>

Electricity Production from Steam-Exploded Corn Stover Biomass

ARTICLE *in* ENERGY & FUELS · MAY 2006

Impact Factor: 2.79 · DOI: 10.1021/ef060033l

CITATIONS

98

READS

85

3 AUTHORS, INCLUDING:



Bruce E Logan

Pennsylvania State University

458 PUBLICATIONS 33,350 CITATIONS

SEE PROFILE

Electricity Production from Steam-Exploded Corn Stover Biomass

Yi Zuo,[†] Pin-Ching Maness,[‡] and Bruce E. Logan^{*,†}

Department of Civil and Environmental Engineering, Penn State University,
University Park, Pennsylvania 16802, and National Renewable Energy Laboratory,
Golden, Colorado 80401

Received January 23, 2006. Revised Manuscript Received April 24, 2006

Electricity generation using microbial fuel cells (MFCs) was examined from corn stover waste biomass using samples prepared through either neutral or acid steam-exploded hydrolysis processes that convert the hemicellulose to soluble sugars. Maximum power densities in fed-batch tests using an air-cathode MFC were 371 ± 13 mW/m² and 367 ± 13 mW/m² for the neutral and acid hydrolysates (1000 mg-COD/L, 250 Ω). Power output exhibited saturation kinetics with respect to fuel concentration, with predicted maximum power densities of $P_{\max} = 475$ mW/m² and half-saturation constants of $K_s = 347$ mg/L (neutral) and $P_{\max} = 422$ mW/m² and $K_s = 170$ mg/L (acid). Coulombic efficiencies (CEs) were comparable to that found using carbohydrates in this type of MFC, with values ranging from 20 to 30% for both hydrolysates. All sugars (monomeric or oligomeric) were completely utilized, with overall biochemical oxygen demand (BOD) removal efficiencies of $93 \pm 2\%$ (neutral) and $94 \pm 1\%$ (acid). Power output could be increased by using a cathode containing a diffusion layer, resulting in maximum power densities of 810 ± 3 mW/m² (neutral) and 861 ± 37 mW/m² (acid). Power was further increased by increasing solution conductivity to 20 mS/cm, resulting in 933 mW/m² (neutral) and 971 mW/m² (acid) for the two hydrolysates. Additional increases in solution conductivity lowered the anode potential and did not increase power. These results demonstrate the potential for a new method of renewable energy production based on conversion of biomass to electricity using MFCs.

Introduction

Corn stover is currently the largest waste biomass resource in the United States, consisting of more than one-third of the total solid waste produced, including municipal solid waste.¹ An estimated 250 million dry tons of corn stover is produced annually.² Only a small amount of corn stover is reused as animal feed or bedding, with >90% left unused in fields.¹ Corn stover typically contains 70% cellulose and hemicellulose and 15–20% lignin.³ The hemicellulose components can be converted to monomeric and oligomeric sugars by a steam-explosion process, forming a sugar-enriched liquid hydrolysate fraction. Ethanol can be recovered from the steam-exploded biomass liquid, but <47% of carbohydrates can be converted to ethanol.⁴ Hydrogen can be produced from the liquefied hemicellulose at an overall utilization efficiency of 87–94% of the glucan and xylan, respectively,⁵ but most of the chemical

oxygen demand (COD) remains as fermentation end products consisting primarily of acetic and butyric acids.⁶

Microbial fuel cells (MFCs) represent a new method for energy production and organic matter degradation. Electrochemically active bacteria oxidize organic matter at the anode surface, releasing electrons and protons. Those electrons are transferred from the anode to the cathode through an external circuit, while the protons move to the cathode directly through solution. At the cathode, oxygen or other chemicals such as ferricyanide accept the electrons. MFCs can be used to generate electricity from various carbohydrates, including low-molecular sugars such as glucose,^{7–9} and complex carbohydrates and carbohydrate-containing wastewaters such as sucrose, starch, molasses, and wastewater from food (cereal) processing plants.^{10–13} The energy conversion based on Coulombic efficiency (CE), or the percent of electrons recovered from the

* Corresponding author. Phone: (814) 863-7908. Fax: (814) 863-7304. E-mail: blogan@psu.edu.

[†] Penn State University.

[‡] National Renewable Energy Laboratory.

(1) Glassner, D. A.; Hettenhaus, J. R.; Schechinger, T. M. Corn stover potential: Recasting the corn sweetener industry. In *Perspectives on new crops and new uses*; Janick, J., Ed.; ASHS Press: Alexandria, VA, 1999; pp 74–82.

(2) Atchison, J. E.; Hettenhaus, J. R. *Innovative methods for corn stover collecting, handling, storing and transporting*; NREL/SR-510-33893; National Renewable Energy Laboratory: Golden, CO, 2004.

(3) Glassner, D. A.; Hettenhaus, J. R.; Schechinger, T. M. Corn stover collection project. *Proceedings of Bioenergy '98: Expanding Bioenergy Partnerships*; Madison, WI, 1998; pp 1100–1110.

(4) Lynd, L. R. Overview and evaluation of fuel ethanol from cellulosic biomass. *Annu. Rev. Energy Environ.* **1996**, *21*, 403–465.

(5) Datar, R.; Huang, J.; Maness, P. C.; Mohagheghi, A.; Czernik, S.; Chornet, E. Hydrogen production from the fermentation of corn stover biomass pretreated with a steam explosion process. *Intl. J. Hydrogen Energy* **2005**, manuscript submitted for publication.

(6) Logan, B. E. Biologically extracting energy from wastewater: Biohydrogen production and microbial fuel cells. *Environ. Sci. Technol.* **2004**, *38*, 160A–167A.

(7) Liu, H.; Logan, B. E. Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environ. Sci. Technol.* **2004**, *38*, 4040–4046.

(8) Rabaey, K.; Lissens, G.; Siciliano, S. D.; Verstraete, W. A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. *Biotechnol. Lett.* **2003**, *25*, 1531–1535.

(9) Chaudhuri, S. K.; Lovley, D. R. Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. *Nat. Biotechnol.* **2003**, *21*, 1229–1232.

(10) He, Z.; Minter, S. D.; Angenent, L. T. Electricity generation from artificial wastewater using an upflow microbial fuel cell. *Environ. Sci. Technol.* **2005**, *39*, 5262–5267.

(11) Min, B.; Logan, B. E. Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell. *Environ. Sci. Technol.* **2004**, *38*, 5809–5814.

(12) Niessen, J.; Schroder, U.; Scholz, F. Exploiting complex carbohydrates for microbial electricity generation—abacteria fuel cell operating on starch. *Electrochem. Commun.* **2004**, *6*, 955–958.

organic matter, varies widely and is a function of the wastewater and type of MFC. Using a single-chamber MFC containing an air-cathode, the CE was 40–55% when a proton-exchange membrane (PEM) was used, but the CE was only 9–12% without the PEM due to oxygen diffusion into the anode chamber.⁷ In contrast, CEs of 83% and 89% have been obtained using two-chamber aqueous-cathode systems containing a PEM.^{8,9} Very low CEs have been found even with two-chamber MFCs containing a PEM, with values of 8.1% for an artificial sucrose solution¹⁰ and 27% for a cereal-processing wastewater.¹³

In this study, we investigated whether MFCs could be used for electricity production from corn stover hydrolysates. While it seemed reasonable that this sugar-enriched material could be used, the power densities produced with this material, relative to those obtained with other pure compounds and wastes, were not known. Power densities were examined using a single-chamber, air-cathode MFC lacking a PEM that has been previously shown to produce 494 mW/m² (CE = 9–12%) with glucose and 146 mW/m² (CE = 20%) with domestic wastewater.⁷ This same system with a PEM produced maximum power densities of only 262 mW/m² (CE = 40–55%) with glucose and 28 mW/m² (CE = 28%) with domestic wastewater.⁷ Performance of the MFC with two different corn stover hydrolysates was evaluated in terms of power density, CE, biochemical oxygen demand (BOD)/COD removal, and color removal. To try to increase power production using these substrates, two methods were tested that have been shown to increase power in this system: increasing the solution conductivity and using a new type of cathode coating (diffusion layer).

Experimental Section

Corn Stover Pretreatment via Steam Explosion. Corn stover was soaked in water (neutral pretreatment) or in 1.2% (w/v) sulfuric acid (acidic pretreatment) for ca. 2 h. After draining and pressing out the residual water, approximate corn stover samples (1 400 g for neutral, 2 500 g for acid) were treated with high-pressure steam in a 4-L steam-explosion reactor¹⁴ at final temperatures and residence times of 220 °C and 3 min (neutral) or 190 °C and 2 min (acid). After cooling, the solids were filtered and washed with water to collect the hemicellulose-derived hydrolysates (3 L for neutral, 4 L for acid). Both hydrolysates were subjected to an overliming process,¹⁵ during which Ca(OH)₂ was added to remove the lignin-derived phenolics, followed by adjusting the final pH to near 7.0. The organic matter concentration of the acid hydrolysate (82 200 ± 4 400 mg-COD/L) was originally 1.65 times larger than that of the neutral hydrolysate (49 900 ± 2 300 mg-COD/L) (Table 1). Before being used in tests, the samples were diluted to the same initial COD concentration (250–1 000 mg-COD/L, as indicated) using a buffered nutrient medium¹⁶ (pH = 7.0) containing the following: NH₄Cl (0.31 g/L), KCl (0.13 g/L), NaH₂PO₄·H₂O (2.93 g/L), Na₂HPO₄ (4.09 g/L), and metal

Table 1. Composition of Acid and Neutral Corn Stover Hydrolysates

component		neutral	acid
glucose (g/L):	total	2.28	9.83
	free	0.00	8.28
xylose (g/L):	total	20.87	32.88
	free	2.20	29.68
galactose (g/L):	total	1.26	2.72
	free	0.35	2.88
arabinose (g/L):	total	1.97	4.53
	free	0.72	4.83
mannose (g/L):	total	0.94	1.58
	free	0.52	1.87
free lignin (g/L)		17.54	nd ^a
pH		6.56	6
conductivity (mS/cm)		9.4	8.0

^a nd, not determined.

(12.5 mL) and vitamin (12.5 mL) solutions. The conductivity was adjusted to 10 mS/cm using NaCl, because solution conductivity has been shown to affect the maximum power density in this type of MFC.¹⁷

MFC Construction. Two single-chamber, membrane-free MFCs were used in this study; they consist of an anode and a cathode placed on opposite sides of a plastic cylindrical chamber (effective volume of 28 mL), as previously described.⁷ The distance between the two electrodes was 4 cm, with each electrode having a projected surface area of 7.1 cm². The anode electrode was made of plain Toray carbon paper (without wet proofing; E-Tek, U.S.A.). Unless stated otherwise, the cathode was made of carbon cloth with 0.5 mg/cm² of Pt on one side (20% of Pt/C catalyst, with water proofing, Vulcan XC-72, De Nora North America, Inc.).

MFC Tests. MFCs were inoculated with domestic wastewater (5 mL, ~300 mg-COD/L) and a nutrient medium¹⁶ (23 mL) containing glucose (1 g/L). Following stable power generation from glucose (after 5 batch cycle operations, 140 h), the substrate was switched to a medium containing a corn stover hydrolysate. The system was considered to be operating under steady-state conditions when the maximum voltage output of one batch cycle was reproducible after filling the reactor with fresh medium at least two times. The medium in the reactor was refilled when the voltage dropped below ~20 mV (resistances of 40–500 Ω) or ~40 mV (1 000–3 000 Ω).

A series of experiments were conducted to study the effects of substrate concentration (250, 450, 800, and 1 000 mg-COD/L) and circuit resistance (40–3 000 Ω) on electricity production. For each initial substrate concentration (250, 450, 800, and 1 000 mg-COD/L), different circuit resistances (40–3 000 Ω) were used to measure the corresponding voltage output and power density for determination of polarization and power density curves. The optimal resistance was then determined as the resistance at which the power density–current density curve of each substrate concentration achieved the peak value. The performance of the reactor at a high COD concentration was then examined in terms of Coulombic efficiency, organic matter degradation, color removal, and final total suspended solids (TSS) concentration of the effluent.

To increase power output, two different approaches were used. First, the solution conductivity was increased from 10 to 40 mS/cm using NaCl, because increases in the solution conductivity have been shown to increase power density in an MFC using glucose as the substrate.¹⁷ An increase in the

(13) Oh, S.; Logan, B. E. Hydrogen and electricity production from a food processing wastewater using fermentation and microbial fuel cell technologies. *Water Res.* **2005**, *39* (19), 4673–4682.

(14) Tucker M. P.; Kim K. H.; Newman M. M.; Nguyen Q. A. Effects of temperature and moisture on dilute-acid steam explosion pretreatment of corn stover and cellulase enzyme digestibility. *Appl. Biochem. Biotechnol.* **2003**, *105–108*, 165–177.

(15) Martinez A.; Rodriguez M. E.; York S. W.; Preston J. F.; Ingram L. O. Effects of Ca(OH)₂ treatments (“overliming”) on the composition and toxicity of bagasse hemicellulose hydrolysates. *Biotechnol. Prog.* **2001**, *17*, 287–293.

(16) Lovley, D. R.; Phillips, E. J. P. Novel mode of microbial energy metabolism: Organic carbon coupled to dissimilatory reduction of iron or manganese. *Appl. Environ. Microbiol.* **1988**, *54* (6), 1472–1480.

(17) Liu, H.; Cheng, S.; Logan B. E. Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature and reactor configuration. *Environ. Sci. Technol.* **2005**, *39*, 5488–5493.

maximum power density with solution conductivity demonstrates that power generation is limited by the solution chemistry and not by bacterial kinetics. Second, the carbon cloth cathode was coated on the air-facing side with a diffusion layer, according to the procedure of Cheng et al.¹⁸ The diffusion layer coating consists of a carbon/poly(tetrafluoroethylene) (PTFE) base layer containing carbon powder (Vulcan XC-72) and PTFE (30 wt % solution), and four overlying layers of PTFE (60 wt % solution).¹⁸

Analytical Techniques. All samples were collected and analyzed when voltage output of each batch cycle was reduced to less than ~20 mV (40–500 Ω resistors) or ~40 mV (1 000–3 000 Ω). Chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solid (TSS), and color of the samples were measured according to standard methods.¹⁹ Samples were centrifuged (Eppendorf centrifuge 5403; 2 750 \times g, 20 min) for soluble COD (SCOD) tests and filtered using 0.2 μ m pore-diameter cellulose syringe filters (Corning) to remove bacteria before color measurement.

Samples analyzed for the concentration of sugar and volatile fatty acids (VFAs) were centrifuged (Eppendorf centrifuge 5403; 2750 \times g, 20 min), and the supernatant was filtered through 0.2 μ m pore-diameter nylon syringe filters (Acrodisc) immediately before analysis. To quantify total sugars, samples were first hydrolyzed in 2.4% (w/v) H_2SO_4 at 121 $^\circ\text{C}$ (148 kPa) for 1 h to convert oligomeric sugars into monomeric sugars.²⁰ After neutralization with calcium carbonate solid and filtration through 0.45 μ m filters, the hydrolyzed samples were then analyzed using high-pressure liquid chromatography (HPLC; Agilent 1090 system, Palo Alto, CA) using a refractive index detector and an HPX-87P lead-based column and deashing guard column (Biorad, CA) at 85 $^\circ\text{C}$. Deionized water was used as the mobile phase at a flow rate of 0.6 mL/min. Monomeric sugars were determined similarly without the acid-hydrolysis step. VFAs in the spent medium were analyzed with an HPLC (Agilent 1050 System, Palo Alto, CA) equipped with a UV detector set at 215 nm (Aminex HPX-87H column, Biorad, CA) at 45 $^\circ\text{C}$, at a flow rate of 0.6 mL/min using 4 mM H_2SO_4 mobile phase. The detection limit for VFAs measurement was 0.1 mM.

Calculations. Voltage (V) was measured across an external resistor using a multimeter with a data-acquisition system (2700, Keithly, U.S.A.). Current (I) was calculated from $I = V/R$ and power (P) according to $P = IV$, where R is the external circuit resistance. Power and current density were normalized by the projected area of the anode (7.1 cm^2). Electrode potentials were measured using a multimeter (83 III, Fluke, U.S.A.) and a reference electrode (Ag/AgCl; RE-5B, Bioanalytical Systems, U.S.A.). The Coulombic efficiency was calculated by comparing the actual coulombs produced (calculated by integrating the current over time) to the theoretical coulombs production based on the measured total COD removal, assuming a conversion factor of 8 g of COD per mole of electrons, and Faraday's constant (96 485 C per mole of electrons). Energy recovery was calculated by comparing the actual power produced (integrating power output over time) to the theoretical energy contained in the consumed substrates (based on total COD removal), assum-

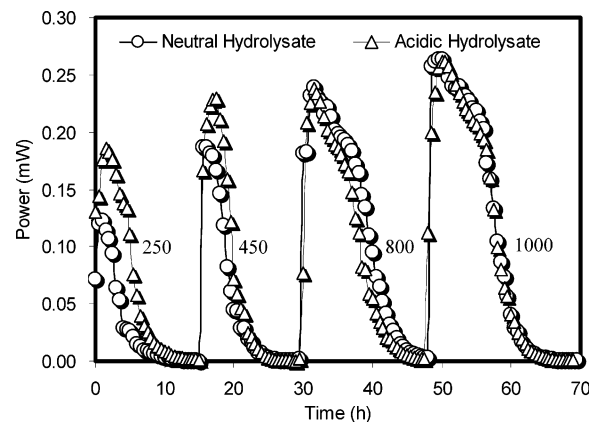


Figure 1. Power generated using neutral or acid hydrolysates at different COD concentrations (250, 450, 800, and 1000 mg-COD/L as indicated).

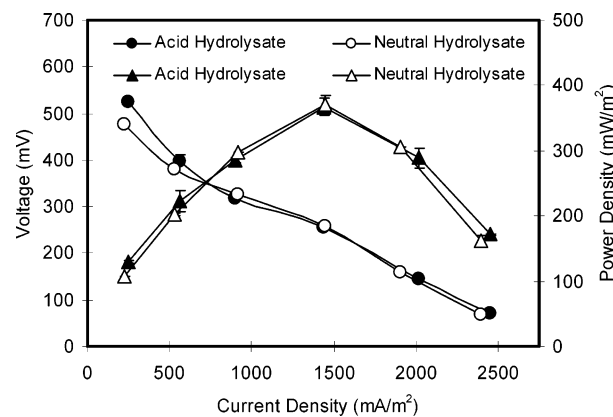


Figure 2. Power density and voltage as a function of current density obtained by varying the external circuit resistance (40–3 000 Ω) at a fixed substrate concentration of 1 000 mg-COD/L. (Error bars \pm SD based on averages measured during highest power output in two separate batch experiments).

ing a conversion factor of 1.07 g-COD/g-glucose, and an enthalpy change of -2801 kJ/mol-glucose under standard conditions.¹⁹

Results

Power Produced Using Corn Stover Hydrolysates. A repeatable cycle of power generation was immediately generated after switching from the glucose medium to either the neutral or acid hydrolysate (Figure 1). Polarization curves obtained by varying the external circuit resistance (40–3 000 Ω) showed that maximum power densities were the same for both hydrolysates at a COD = 1 000 mg/L, with 371 ± 13 mW/m^2 obtained for the neutral hydrolysate (current density of 1 446 mA/m^2 , $R = 250$ Ω) and 367 ± 13 mW/m^2 obtained for the acid hydrolysate (1 439 mA/m^2 , 250 Ω) (Figure 2).

The maximum power obtained at different initial COD concentrations fit a Monod type of curve. The predicted maximum power density for the neutral hydrolysate was $P_{\text{max}} = 475$ mW/m^2 , with a half-saturation constant of $K_s = 347$ mg/L ($R^2 = 0.990$). For the acid hydrolysate, the predicted maximum power density was similar ($P_{\text{max}} = 422$ mW/m^2), but the half-saturation constant ($K_s = 170$ mg/L) ($R^2 = 0.999$) was nearly half that obtained with the neutral hydrolysate (Figure 3). A lower half-saturation constant K_s showed that the acid hydrolysate could produce more power than the neutral hydrolysate at the same lower substrate concentration.

Organic Matter Degradation. After a complete cycle of power generation, sugars (monomeric or oligomeric) were found

(18) Cheng, S.; Liu, H.; Logan, B. E. Increased power and Coulombic efficiency of single-chamber microbial fuel cells through an improved cathode structure. *Electrochem. Commun.* **2006**, 8, 489–494.

(19) American Public Health Association, American Water works association, Water Pollution Control Federation. *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; American Public Health Association: Washington, DC, 1995.

(20) Ruiz R.; Ehrman, T. *NREL Analytical Procedure, No. 014*; National Renewable Energy Laboratory, Golden, CO, 1996.

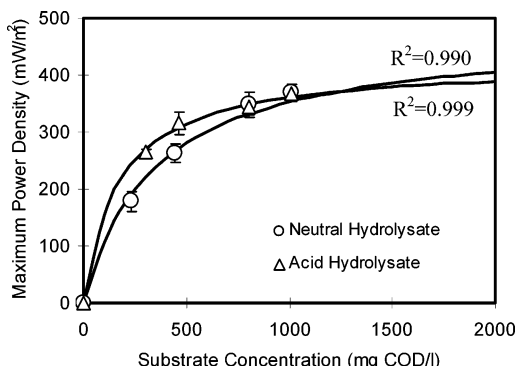


Figure 3. Maximum power density as a function of initial substrate concentration. (Error bars \pm SD based on averages obtained during highest power output in three or more separate batch experiments).

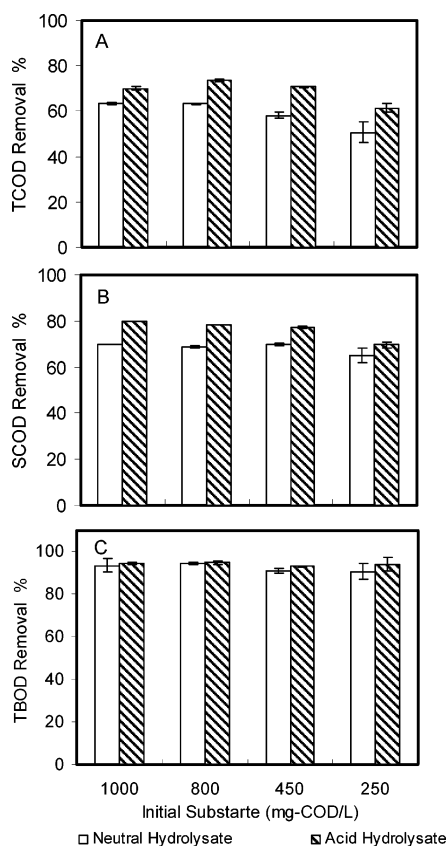


Figure 4. Organic matter removal efficiency in terms of total and soluble COD, and total BOD as a function of initial substrate concentration. (Error bars are \pm SD based on samples analyzed in duplicate (TCOD and SCOD) or triplicate (TBOD)).

to be completely degraded. In addition, there were no detectable volatile organic acids (acetic, lactic, formic, propionic, and butyric) in solution. Total COD removal efficiencies ranged from 60 to 70%, while soluble COD removals were $68 \pm 2\%$ and $76 \pm 5\%$ for the neutral and acid hydrolysates, respectively (Figure 4 parts A and B). BOD removal efficiencies were $93 \pm 2\%$ (neutral) and $94 \pm 1\%$ (acid) (Figure 4C).

The physical characteristics of the liquid following a complete cycle of power generation were examined. TSS concentrations of the effluents increased in proportion to initial substrate concentration, with different production rates for the neutral hydrolysate (0.09 ± 0.01 mg-TSS/mg-COD-removed) and the acid hydrolysate (0.06 ± 0.00 mg-TSS/mg-COD-removed) (Figure 5A). The color removal efficiencies for both hydrolysates increased with initial substrate concentration. At the highest

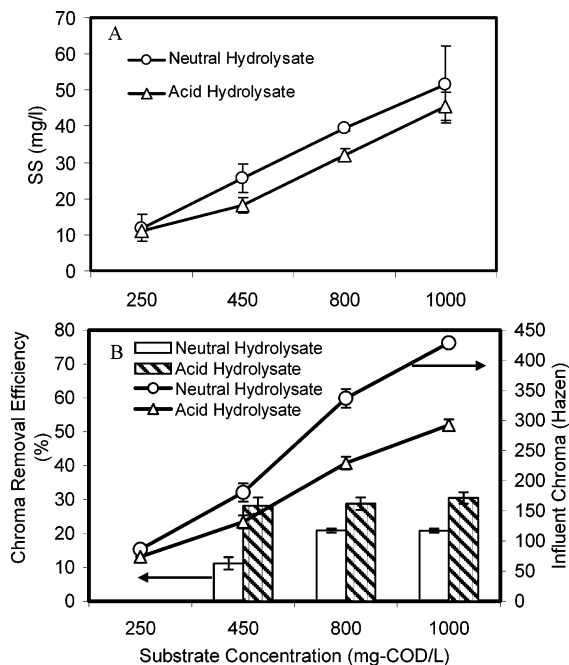


Figure 5. Physical characteristics of effluents in terms of TSS concentration and chroma removal as a function of initial substrate concentration. [Error bars are \pm SD based samples analyzed in duplicate (chroma removal and influent chroma) or triplicate (TSS)].

substrate concentration of 1 000 mg-COD/L, the neutral and acid hydrolysates initially had 430 and 290 chroma units (Hazen). The effluents for the neutral and acid hydrolysates had 340 and 200 chroma units, achieving removal efficiencies of 21 and 30%, respectively (Figure 5B). At the lowest substrate concentration of 250 mg-COD/L, the influents for both hydrolysates were much lower, with color intensities of 85 (neutral) and 75 (acid) chroma units, and there was no measurable color removal.

Coulombic Efficiency. The overall Coulombic efficiency was a function of either substrate concentration or external circuit resistance. When initial substrate concentration increased from 250 to 1 000 mg-COD/L, at the fixed optimal external resistances, the CE decreased slightly from 29.5 to 23.3% for the neutral hydrolysate and from 25.6 to 19.3% for the acid hydrolysate (Figure 6A). At a fixed initial substrate concentration (1 000 mg-COD/L), but at different external resistances, the CE varied over a wider range and there was an almost linear increase in the CE with current density. The CE increased from 14.2 to 29.2% with current density from 534 to 2390 mA/m² for the neutral hydrolysate and from 12.3 to 26.9% with current from 560 to 2460 mA/m² for the acid hydrolysate (Figure 6B).

Improving Power Output. By adding a diffusion layer to the cathode, the maximum power produced for the neutral and acid hydrolysates (1 000 mg-COD/L) increased by more than 100%. For the neutral hydrolysate, maximum power density increased from 371 ± 13 mW/m² (1 446 mA/m²) to 810 ± 3 mW/m² (2 137 mA/m²). The maximum power for the acid hydrolysate increased slightly more, from 367 ± 13 mW/m² (1 439 mA/m²) to 861 ± 37 mW/m² (2 202 mA/m²) (Figure 7).

When solution conductivity was increased from 10 to 20 mS/cm, maximum power densities for both neutral and acid hydrolysates increased to 933 and 971 mW/m², respectively (Figure 8A). However, when the solution conductivity was increased to 30 or 40 mS/cm, the maximum power densities decreased. At a solution conductivity of 40 mS/cm, maximum

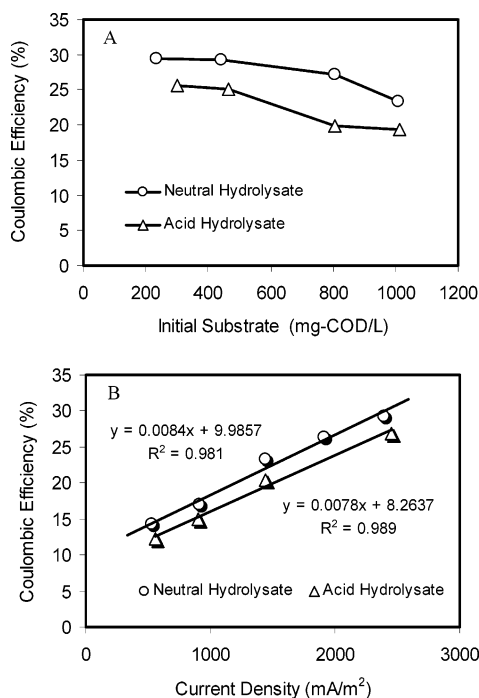


Figure 6. Coulombic efficiencies as a function of (A) initial substrate concentration and (B) current density.

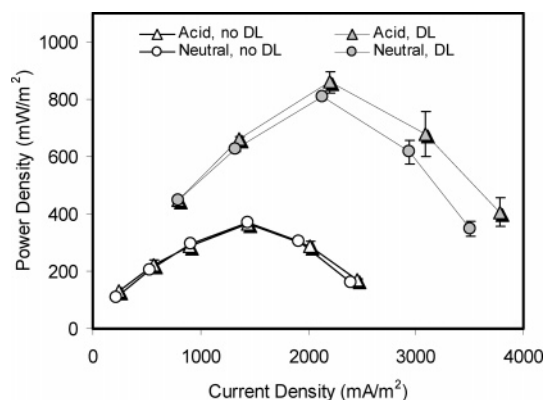


Figure 7. Effect of a cathode diffusion layer (DL) on maximum power densities as a function of current density. (Error bars \pm SD based on average power output in two separate batch experiments).

power densities decreased to 674 mW/m² for the neutral hydrolysate and to 743 mW/m² for the acid hydrolysate. These values were lower than those obtained at a solution conductivity of 10 mS/cm (Figure 8A).

It has previously been shown that the increase of solution conductivity will decrease the internal resistance,¹⁷ which decreases the ohmic potential loss and can increase the cell voltage and power output if the system is not limited by bacterial kinetics (i.e., the rate at which the substrate can be degraded). To understand the adverse effect of conductivity on power, the working potentials of the anode and cathode were examined using a multimeter and a reference electrode located in the middle of the fuel cell chamber (acid hydrolysate, 1000 mg-COD/L). When solution conductivity increased from 10 mS/cm (equivalent to 0.6% NaCl) to 20 mS/cm (equivalent to 1.2% NaCl), the anode working potential remained essentially constant but the cathode potential increased, resulting in a greater overall circuit voltage and power density (Figure 8B). When solution conductivity was increased to 30 or 40 mS/cm (1.8 and 2.4% NaCl), the anode working potential increased while the cathode working potential remained relatively stable, resulting in a lower

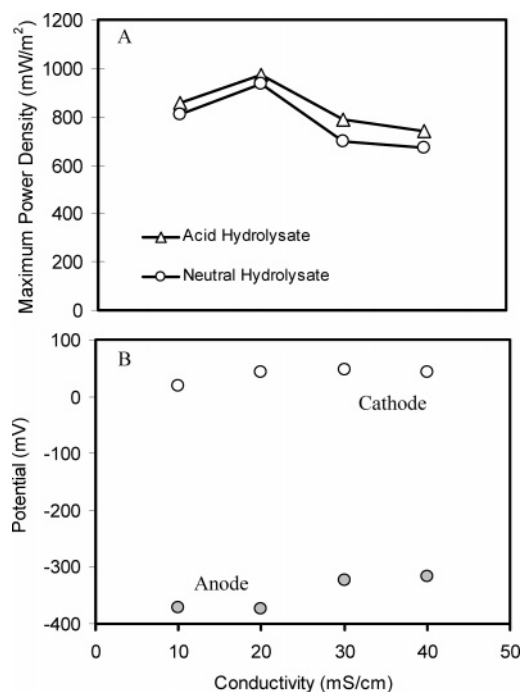


Figure 8. Effect of conductivity (10–40 mS/cm) on (A) maximum power densities and (B) electrode potentials using acid corn stover hydrolysate (vs Ag/AgCl reference electrode; 195 mV vs NHE).

overall voltage and power density. This increase in the anode working potential demonstrated that the activity of the electrochemically active bacteria on the anode surface was inhibited by solution conductivities of 30 or 40 mS/cm.

Discussion

Electricity was generated using both the neutral and acid corn stover hydrolysates with maximum power densities similar to the highest power densities achieved in same MFCs using pure compounds. The predicted maximum power densities achieved here were 475 and 422 mW/m² for the neutral and acid hydrolysates, respectively. The same MFC system produced 494 mW/m² with glucose,⁷ while power output was lower (349 mW/m²) with butyrate and domestic wastewater (146 mW/m²).^{7,21} Adding a diffusion layer to the cathode increased the maximum power density to 810 ± 3 mW/m² (neutral) or 861 ± 37 mW/m² (acid) (1000 mg-COD/L), respectively. These values are similar to the maximum power density of 800 mW/m² found with glucose using this modified cathode.¹⁸ These comparisons demonstrate for the first time that waste materials can produce power densities similar to those obtained with pure compounds. Our findings also indicate that the microbial consortium in the wastewater inoculum can utilize both the oligomeric sugars in the neutral hydrolysate and the monomeric sugars in the acid hydrolysate equally well for power generation. Thus, the acid is not required for the steam-explosion process, simplifying the biomass pretreatment process needed for power generation in an MFC.

While modifying the cathode increased power in a manner similar to that previously described using glucose,¹⁸ increasing solution conductivity to 30 mS/cm or more did not increase the maximum power. The greatest power density achieved here was 971 mW/m² for acid hydrolysate at a medium conductivity

(21) Liu, H.; Cheng, S.; Logan, B. E. Production of electricity from acetate or butyrate in a single chamber microbial fuel cell. *Environ. Sci. Technol.* **2005**, *39*, 658–662.

of 20 mS/cm (equivalent to 1.2% NaCl), but this decreased to 789 mW/m² at 30 mS/cm. Liu et al.¹⁷ found that increasing the solution conductivity to 40 mS/cm (using NaCl) increased power output with acetate up to 1330 mW/m² in the same type of MFC. Oh and Logan²² also found, using a two-chamber MFC, that maximum power was increased with solution conductivities up to 40 mS/cm (using KCl) but power decreased at higher solution conductivities. The decrease in the power output at high solution conductivities shown here was due to the increased working potential of the anode, which resulted in a lower circuit voltage. While the bacterial activity here was reduced by the higher salt concentration, it may be possible to overcome this limitation in future tests by gradual acclimation of the culture to higher salt concentrations.

Efficiency of Organic Matter Removal. The conversion of organic matter to electricity, on the basis of BOD removal, was relatively high with >93% of the BOD removed for both hydrolysates. This BOD removal efficiency was much higher than that found for domestic wastewater (78 ± 2%),²³ indicating the relatively good biodegradability of the high-sugar content hydrolysates. The lack of complete BOD removal was likely due to more slowly degraded nonsugar components of the hydrolysates or compounds that could not be degraded under anaerobic conditions. While all sugars (oligomeric or monomeric) were completely utilized during in-batch tests, the hydrolysates also contained soluble lignin and small amounts of furfural and hydroxymethyl furfural (HMF). That latter material contributed to the remaining COD and likely some of the remaining BOD. The overall COD removal efficiencies were only 60% and 70% for neutral and acid hydrolysates, respectively.

Implications for Using Corn Stover as a Source of Renewable Energy. These studies demonstrate that there is great potential for electricity generation using corn stover biomass. Such energy production could be important as a result of the large amount of this material generated, estimated to be 150 million tons per year.³ Assuming all the carbohydrates in the corn stover (70% by mass)⁵ can be completely hydrolyzed to glucose (neglecting the energy input for the corn stover hydrolysis process), and that they are all removed in the MFC process at an energy recovery of 10% (the maximum obtained here), 4.6 × 10¹⁰ kWh/year could be produced, equal to 52 power plants generating 100 MW each, worth \$6.9 billion per year (assumes \$0.15/kWh²⁴). There are obviously many technical challenges to be faced in achieving renewable energy using

this waste resource separate from the specific technology examined here, such as reducing the cost for the collection and transportation of corn stover from the field, minimizing the energy expended for the steam-explosion hydrolysis, and scaling up the process in an economical manner. In addition, energy recovery in the MFC process needs to be improved to be competitive with other more-mature technologies, such as ethanol production (47% efficiency)⁴ and anaerobic digestion in combination with combustion (25–35% efficiency). However, the current study suggests that, even with modest capture efficiencies of the energy in this waste biomass, a substantial amount of electricity could be generated from this material. Further research should be conducted to examine methods to increase the efficiency of BOD removal, color removal, and the Coulombic efficiency using corn stover hydrolysates in MFCs.

Conclusions

The feasibility of electricity generation from corn stover waste biomass was demonstrated using single-chamber, air-cathode MFCs and diluted corn stover hydrolysates. It was shown that the maximum power densities of 371 ± 13 mW/m² and 367 ± 13 mW/m² were similar for the neutral and acid corn stover hydrolysates (1 000 mg-COD/L, 250 Ω), respectively, using a standard air-cathode. However, power output was increased by using a newly developed cathode coating (diffusion layer) to 810 ± 3 mW/m² for the neutral hydrolysate and to 861 ± 37 mW/m² using the acid hydrolysate. Additional increases in maximum power densities were possible by increasing the solution conductivity to 20 mS/cm, resulting in 933 mW/m² (neutral) and 971 mW/m² (acid). All sugars (monomeric or oligomeric) were completely utilized, with overall BOD removal efficiencies of 93 ± 2% (neutral) and 94 ± 1% (acid). From these lab results, it was concluded that corn stover hydrolysates have an excellent potential to be used as substrates for renewable and sustainable electricity generation with MFC technologies.

Acknowledgment. The authors thank D.W. Jones (Penn State) and J. Sluiter (NREL) for help with analytical measurements and Dr. S. Czernik (NREL) for the biomass mass balance analysis. This research was supported by National Science Foundation Grant BES-0401885, the Natural Resources Conservation Service of the United States Department of Agriculture Grants 68-3A75-3-150, and the Paul L. Busch Award (to B.E.L.) by the Water Environment Research Foundation.

EF060033L

(22) Oh, S.; Logan, B. E. Proton exchange membrane and electrode surface areas as factors that affect power generation in microbial fuel cells. *Appl. Microbiol. Biotechnol.* **2006**, *70*, 162–169.

(23) Liu, H.; Ramnarayanan, R.; Logan, B. E. Production of electricity during wastewater treatment using a single chamber microbial fuel cell. *Environ. Sci. Technol.* **2004**, *38*, 2281–2285.

(24) 2003 California Average Retail Electricity Rates by Major Utility. Access date: Sept 8, 2005. http://www.energy.ca.gov/electricity/current_electricity_rates.html.