

Short communication

Electricity production from twelve monosaccharides using microbial fuel cells

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Abstract

Direct generation of electricity from monosaccharides of lignocellulosic biomass was examined using air cathode microbial fuel cells (MFCs). Electricity was generated from all carbon sources tested, including six hexoses (D-glucose, D-galactose, D(–)-levulose (fructose), L-fucose, L-rhamnose, and D-mannose), three pentoses (D-xylose, D(–)-arabinose, and D(–)-ribose), two uronic acids (D-galacturonic acid and D-glucuronic acid) and one aldonic acid (D-gluconic acid). The mixed bacterial culture, which was enriched using acetate as a carbon source, adapted well to all carbon sources tested, although the adaptation times varied from 1 to 70 h. The maximum power density obtained from these carbon sources ranged from 1240 ± 10 to 2770 ± 30 mW m⁻² at current density range of 0.76–1.18 mA cm⁻². D-Mannose resulted in the lowest maximum power density, whereas D-glucuronic acid generated the highest one. Coulombic efficiency ranged from 21 to 37%. For all carbon sources tested, the relationship between the maximum voltage output and the substrate concentration appeared to follow saturation kinetics at 120 Ω external resistance. The estimated maximum voltage output ranged between 0.26 and 0.44 V and half-saturation kinetic constants ranged from 111 to 725 mg L⁻¹. Chemical oxygen demand (COD) removal was over 80% for all carbon sources tested. Results from this study indicated that lignocellulosic biomass-derived monosaccharides might be a suitable resource for electricity generation using MFC technology.

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1. Introduction

Recent efforts have been focusing on finding renewable energy alternatives to fossil fuels. The production of fuel and energy from lignocellulosic biomass, such as agricultural residues and woody biomass, has drawn great attention because of the abundance, ready availability and renewable nature of these resources [1,2]. The main components of lignocellulosic biomass are cellulose, hemicelluloses and lignin. While cellulose is a homopolysaccharide consisting of D-glucose, hemicelluloses are branched heteropolysaccharides that are mainly composed of three hexoses (D-glucose, D-galactose, D-mannose), two pentoses (D-xylose and L-arabinose) and uronic

acids such as galacturonic acid and glucuronic acid. Lignocellulosic biomass also contains a small amount of carbohydrates that are derived from the following monosaccharides: L-rhamnose, L-fructose, D-fucose, and D-ribose. Lignin is the most abundant aromatic polymer in nature, and is a complex polymer of phenylpropane units that are cross-linked to each other with a variety of different chemical bonds [3]. Pre-treatments and subsequent hydrolysis of the lignocellulosic biomass into monosaccharides are often essential processes for the production of biofuel such as ethanol and other biochemicals [4]. The composition of the products from pre-treatment and hydrolysis depends on the biomass sources as well as the pre-treatment/hydrolysis methods. Efficient utilization of all pre-treatment/hydrolysis products using relatively simple systems is indispensable for economic conversion of lignocellulosic biomass to energy and fuels [1,5].

Microbial fuel cell (MFC) technology, which uses microorganisms to catalyze the direct generation of electricity from

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organic matter, provides a potential new approach for the generation of renewable energy from biomass [6–8]. MFCs can use bacteria from the natural environment to generate electricity from various substrates such as glucose, acetate, butyrate, lactate, ethanol, cysteine and bovine serum albumin as well as those from waste streams such as domestic wastewaters and various food industry wastewaters [7–14]. It was recently reported that hydrolysates from dilute acid pre-treatment (1.2%, w/v) of corn stover could be used in an MFC for electricity generation [12]. Increased power generation in sediment MFCs was also reported with the addition of biomass, including chitin and cellulose [8]. In our recent study, we dissolved pine wood flour with 10% sulfuric acid solution and found that the resulting hydrolysate could be directly used in an MFC for electricity production (unpublished results). The acid hydrolysates from pine wood or corn stover supposedly contain all monosaccharides previously described. However, it is poorly understood whether all these monosaccharides can be utilized by bacteria in an MFC for electricity generation. The relative power generation capability of these monosaccharides is basically unknown.

In this study, we first investigated the power generation in MFCs from each of the 12 monosaccharides, including six hexoses (D-glucose, D-galactose, D(–)-levulose (fructose), L-fucose, L-rhamnose, and D-mannose), three pentoses (D-xylose, D(–)-arabinose, and D(–)-ribose), two uronic acids (D-galacturonic acid and D-glucuronic acid) and one aldonic acid (D-gluconic acid). We also investigated the Coulombic efficiency (E_c), the removal rate of chemical oxygen demand (COD) of the MFCs, the effects of monosaccharide concentration on the maximum voltage output and half-saturation constant.

2. Materials and methods

2.1. MFC construction

MFCs were constructed as previously described [9]. The volume of the MFC chamber (made of Plexiglas) was 12 mL. The electrodes were placed on opposite sides of the cylindrical chamber with a spacing of 1.7 cm. Non-wet proofed carbon cloth (type A, E-TEK, Somerset, NJ, USA) and wet-proofed (30%) carbon cloths (type B, E-TEK Division, Inc., Somerset, NJ, USA) were used as anode and cathode, respectively. The air-facing side of the cathode was coated with carbon and poly(tetrafluoroethylene) (PTFE) layers, which was prepared according to a published procedure [13]. The water-facing side of the cathode was coated with platinum (0.5 mg cm⁻² cathode area) using Nafion as a binder. For all the MFCs used in this study, the surface areas of the anodes and cathodes were 2.0 and 7.0 cm², respectively. The smaller anodes were used to reduce the limitations from the cathodes.

2.2. Inoculation of a bacterial culture in an MFC and the operation of an MFC

Each of 12 MFCs was inoculated with a mixed bacterial culture that was originally enriched from domestic wastewater and was maintained in our laboratory MFCs that had been oper-

ated for over 1 year using sodium acetate as a carbon source. Preliminary results indicated that the primary constituents of the acclimated mixed cultures were *Rhodococcus* sp. and *Paracoccus* sp. Sodium acetate (2000 mg L⁻¹) was initially used as the carbon source in each MFC with a medium solution containing: NH₄Cl (0.31 g L⁻¹); NaH₂PO₄·H₂O (5.84 g L⁻¹); Na₂HPO₄·7H₂O (15.47 g L⁻¹); KCl (0.13 g L⁻¹); a mineral solution (12.5 mL) and a vitamin solution (12.5 mL) as reported previously [9,14]. The sodium acetate medium solution in each MFC was refreshed when the voltage decreased below 0.05 V. When a stable power output at 1000 Ω was obtained, the sodium acetate solution was replaced with one of the following monosaccharides: 6.7 mM hexoses (D-glucose, D-galactose, D-mannose, D-fructose, L-fucose and L-rhamnose), 8 mM pentoses (D-xylose, D-ribose and L-arabinose), 6.7 mM D-galacturonic acid, D-glucuronic acid, and D-gluconic acid. The different molar concentration of the monosaccharides was chosen in order to standardize the total organic carbon concentration (480 mg L⁻¹) in solution.

Polarization curves were made by varying the external resistance from 1000 to 50 Ω. For each resistance, MFCs ran for at least two batches to ensure that repeatable power output could be achieved. Hourly averaged voltages were used to calculate the power density. Various concentrations of the monosaccharides (150–1400 mg L⁻¹) were also used to investigate the effects of the monosaccharide concentration on the electricity production at a fixed resistance of 120 Ω. Twelve MFCs with each containing a different monosaccharide were run simultaneously in a constant temperature chamber (30 ± 2 °C).

2.3. Analyses and calculations

Voltage was measured using a multimeter with a data acquisition system (2700, Keithly, Cleveland, OH, USA). Power density (mW m⁻²) was calculated according to $P = IV/A$, where I is the current, V voltage, and A the projected area of the anode. E_c is an important parameter in evaluating MFC performance and is described as the percentage of electrons recovered from the organic matter versus the theoretical maximum whereby all electrons are used for electricity production. The E_c was calculated as $E_c = C_P/C_{T1} \times 100\%$, where C_P is the total coulombs calculated by integrating the current over time, C_{T1} is the theoretical amount of coulombs based on the added substrates.

Voltage was modeled as a function of substrate concentration (S) using a Monod-type equation as:

$$V = \frac{V_{\max} S}{K_s + S} \quad (1)$$

where V_{\max} , the maximum voltage and K_s , the half-saturation constant were determined using the Excel Solver (Microsoft, version 2003).

An aqueous sample taken from each MFC at the end of the batch experiment was filtered through a sterile syringe filter (0.22 μm). The filtrate was used for the determination of COD according to a standard method [15]. Comparison of the planktonic bacterial concentrations in the MFC solutions was made by measuring the OD₆₀₀, optical density at 600 nm, using

a 1 cm cuvette, with a spectrophotometer (UV-1700 Pharmaspec, Shimadzu, Japan). Unsterile media were used as blank.

3. Results and discussion

3.1. Adaptation of the bacteria to new substrates

Sodium acetate was used as the carbon source for all 12 MFCs during the start-up period. When a stable power was generated, the culture medium was replaced with a monosaccharide solution. All monosaccharides produced electricity without adding new bacterial inoculum (Fig. 1). However, the adaptation time, which was defined as the time between adding a monosaccharide solution to an MFC and reaching a maximum power output at $1000\ \Omega$, varied for different monosaccharides. The bacteria easily adapted to glucose in less than 1 h (Fig. 1A). A little longer adaptation time was required for gluconic acid (ca. 7 h) compared to glucose (Fig. 1D). While the adaptation time was similar (around 12–18 h) for fructose, galactose,

fructose, mannose, xylose, galacturonic acid, and glucuronic acid under the same conditions (Fig. 1A–D), it was much longer for arabinose (ca. 60–70 h) (Fig. 1C). Once the bacteria adapted to a new monosaccharide, electricity was quickly recovered when the monosaccharide solution was refilled (Fig. 1).

Pure cultures of various electricity-generating bacteria can utilize certain substrates only. For example, the carbon sources that pure *Geobacter* species could use are primarily limited to organic acids, ethanol and aromatic compounds [16,17]. *Pseudomonas* species isolated from the MFC with glucose as carbon source could not further utilize the fermentative products, such as acetate, for electricity generation [7,18]. *Shewanella* species could only incompletely oxidize a limited number of organic acids such as lactate and pyruvate to acetate under anaerobic conditions [16,17], limiting the efficiency of electricity production. Results from this and previous studies appear to suggest that a mixed bacterial culture is superior to a pure bacterial culture in terms of electricity generation, especially when a mixture of carbon sources is used [7,9,12,19].

3.2. Power density curves

The maximum power density of MFCs with each monosaccharide was determined by varying the circuit resistance from 1000 to $50\ \Omega$. For hexoses, glucose resulted in the highest maximum power density of $2160 \pm 10\ \text{mW m}^{-2}$ at a current density of $0.7\ \text{mA cm}^{-2}$, whereas mannose had the lowest one, $1240 \pm 10\ \text{mW m}^{-2}$ (Fig. 2A).

Xylose and arabinose are major pentoses in lignocellulosic biomass while ribose content is fairly low [20,21]. Xylose generated the maximum power density of $2330 \pm 60\ \text{mW m}^{-2}$ at a current density of $0.74\ \text{mA cm}^{-2}$, which was higher than those from arabinose ($2030 \pm 20\ \text{mW m}^{-2}$) and ribose ($1520 \pm 10\ \text{mW m}^{-2}$) (Fig. 2B). In fact, the maximum power density from xylose was even higher than that from glucose. Xylose was reported as one of the major constituents of corn stover acid hydrolysates ($32.88\ \text{g L}^{-1}$) along with glucose ($9.83\ \text{g L}^{-1}$) [12].

Glucuronic acid resulted in a maximum power density of $2770 \pm 30\ \text{mW m}^{-2}$ at a current density of $1.18\ \text{mA cm}^{-2}$, which was 35% higher than that from gluconic acid and 86% higher than that from galacturonic acid. The maximum power density from glucuronic acid was even higher than those provided by glucose and xylose, indicating that glucuronic acid was a good substrate for electricity generation.

3.3. Effect of substrate concentration on electricity generation

For all monosaccharides tested, the maximum voltage output at $120\ \Omega$ external resistance initially increased with the monosaccharide concentration, however, further increases above a certain level did not improve the electricity generation (Fig. 3). The maximum voltage ranged from 0.26 to 0.44 V and a half-saturation constant (K_s) ranged from 110 to $725\ \text{mg L}^{-1}$ ($R^2 = 0.826\text{--}0.995$) (Table 1). Glucose produced

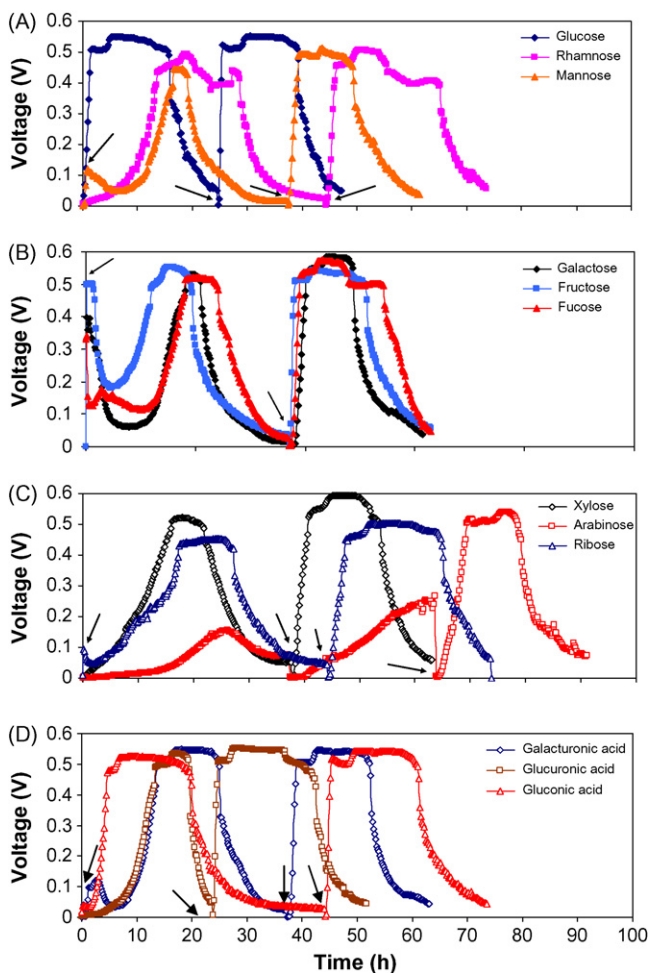


Fig. 1. The start-up process of electricity generation from hexoses (A, B), pentoses (C) and sugar derivatives (D) using a mixed bacterial culture at $1\ \text{k}\Omega$. Acetate was used as an initial carbon source for enrichment. Arrows indicate the addition of new substrates. The initial power generation in B panel was possibly due to the incomplete replacement of the acetate medium solution from the previous batch.

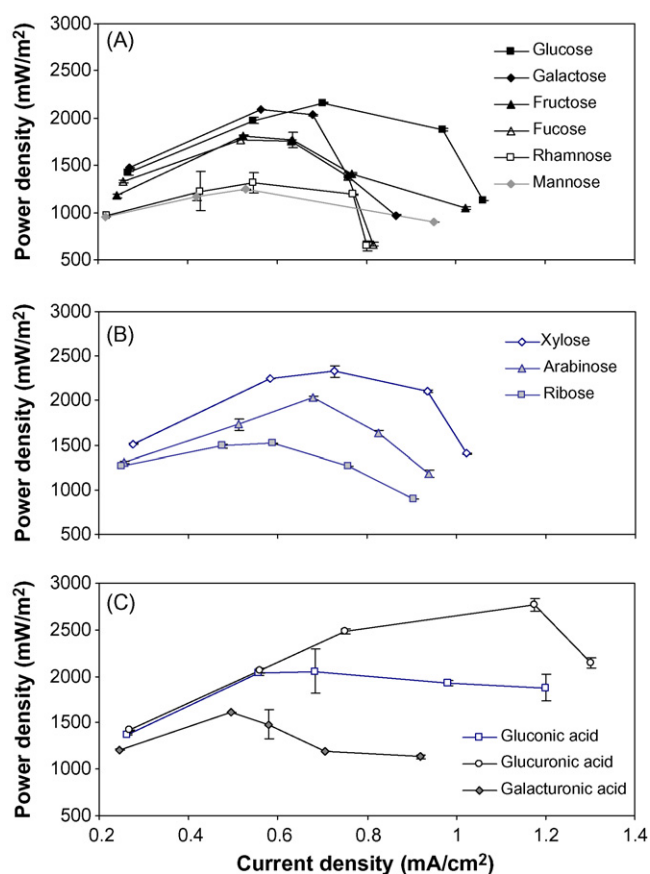


Fig. 2. Power densities as a function of current density using hexoses (A), pentoses (B) and sugar derivatives (C) as carbon sources.

the highest maximum voltage (0.39 V) with $K_s = 637 \text{ mg L}^{-1}$ ($R^2 = 0.993$) and rhamnose produced the lowest voltage (0.27 V) with $K_s = 283 \text{ mg L}^{-1}$ ($R^2 = 0.826$) among the six hexoses tested. Xylose resulted in a higher maximum voltage (0.38 V) than two other pentoses (arabinose and ribose). Although similar half-saturation constants were obtained with xylose and arabinose, a higher power output was achieved with xylose. Glucuronic acid resulted in a higher maximum voltage (0.44 V) with

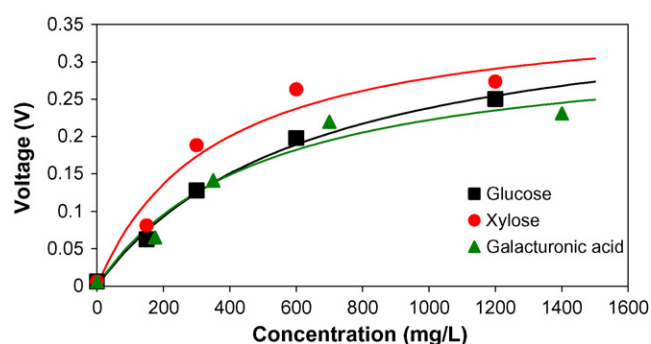


Fig. 3. Effect of substrate concentration on voltage output using different carbon sources at 120 Ω .

$K_s = 725 \text{ mg L}^{-1}$ ($R^2 = 0.987$) than gluconic acid and galacturonic acid (Table 1). The predicted half-saturation constant of gluconic acid was higher than that of galacturonic acid, and a higher maximum power output was obtained with glucuronic acid. The half-saturation constant of glucose from this study was about 5.2 times higher than that from the previous report using the same substrate [9]. The discrepancy was mainly due to the selection of different resistances in these studies. When an MFC is operated at a high external resistance, the electron transfer rate from bacteria to anode could be limited by the external resistance and increasing the substrate concentration will not increase the power output. The reduction of the external resistance from 1000 to 120 Ω allowed us to better evaluate the effect of the monosaccharide concentration on the voltage output of the MFCs tested, since the maximum power outputs occurred at a resistance range of 110–220 Ω for most of the monosaccharides tested in this study.

3.4. Substrate utilization and Coulombic efficiency

About 80–95% of COD was removed for all monosaccharides tested at the end of the experiment when the voltage was lower than 0.05 V (Table 1). However, the E_c that was calculated based on the total substrate concentration was only in the range of 21–37% at 120 Ω , indicating that a substantial

Table 1
The performances of MFCs using different monosaccharides

| | Carbon sources | Power density (mW m^{-2}) | E_c^a (%) | COD removal (%) | OD ₆₀₀ ^b | V_{max} (V) | K_s (mg L^{-1}) | R^2 (%) |
|-------------------|-------------------|--------------------------------------|-------------|-----------------|--------------------------------|----------------------|------------------------------|-----------|
| Hexose | Glucose | 2160 \pm 10 | 28 | 93 \pm 2 | 0.245 | 0.39 | 637 | 0.993 |
| | Galactose | 2090 \pm 10 | 23 | 93 \pm 2 | 0.289 | 0.35 | 403 | 0.960 |
| | Fructose | 1810 \pm 10 | 23 | 88 \pm 2 | 0.180 | 0.31 | 275 | 0.985 |
| | Fucose | 1760 \pm 10 | 34 | 84 \pm 4 | 0.156 | 0.35 | 383 | 0.995 |
| | Rhamnose | 1320 \pm 110 | 30 | 90 \pm 2 | 0.127 | 0.27 | 283 | 0.826 |
| | Mannose | 1240 \pm 10 | 25 | 88 \pm 4 | 0.178 | 0.29 | 322 | 0.974 |
| Pentose | Xylose | 2330 \pm 60 | 31 | 95 \pm 2 | 0.131 | 0.38 | 352 | 0.960 |
| | Arabinose | 2030 \pm 20 | 27 | 93 \pm 2 | 0.069 | 0.26 | 111 | 0.996 |
| | Ribose | 1520 \pm 40 | 30 | 86 \pm 3 | 0.103 | 0.27 | 447 | 0.955 |
| Sugar derivatives | Galacturonic acid | 1480 \pm 150 | 22 | 80 \pm 2 | 0.169 | 0.33 | 493 | 0.964 |
| | Glucuronic acid | 2770 \pm 30 | 24 | 89 \pm 1 | 0.207 | 0.44 | 725 | 0.987 |
| | Gluconic acid | 2050 \pm 30 | 30 | 93 \pm 6 | 0.313 | 0.28 | 580 | 0.963 |

^a Coulombic efficiencies at 120 Ω external resistance.

^b OD₆₀₀ at the end of the last batch.

amount of electrons were lost. Many factors could attribute to the electron loss in the air cathode MFCs, including the electron transfer from substrate to other electron acceptors in solution, such as nitrate, sulfate, and oxygen, and the substrate utilization for bacterial growth, fermentation, and/or methanogenesis [9]. While there was no nitrate in the media, the sulfate concentrations were also quite low (0.35 mmol L^{-1}) in the solution, which would only account for less than 5% of the substrate loss. On the other hand, significant amount of oxygen could be diffused through the membrane-free air cathode and oxidize the substrate by aerobic bacteria [9]. A modification of the single chamber air cathode by adding a cloth layer on the cathode surface significantly reduced the oxygen diffusion and enhanced the E_c in a recent study [22]. Although the cell yield for anaerobic bacteria on anode was generally low compared to aerobic bacteria [7], the growth of the aerobic bacteria on the cathode surface [9] and the anaerobic/aerobic bacteria in the solution may account for a significant portion of the diminishment of the E_c . The bacterial concentrations in solution at the end of the last batch using monosaccharides were all much higher (1.5–4.5-fold) than that using acetate ($\text{OD}_{600\text{nm}} = 0.069$) with only arabinose as exception (0.069) (Table 1). The faster substrate utilization of these monosaccharides for bacteria growth and the relatively lower current density might attribute to the lower E_c of MFCs using monosaccharides compared to that using acetate (59%).

4. Conclusions

Electricity was successfully generated from six hexoses (glucose, galactose, fructose, fucose, rhamnose, mannose), three pentoses (xylose, arabinose, ribose) and three sugar derivatives (galacturonic acid, glucuronic acid, gluconic acid) using a mixed bacterial culture in single-chamber air cathode MFCs. The mixed bacterial culture enriched and maintained with sodium acetate easily adapted to all carbon sources tested with the adaptation time ranging from 1 to 70 h. The maximum power density ranged from 1410 ± 20 to $2760 \pm 40 \text{ mW m}^{-2}$ with glucuronic acid producing the highest power density and mannose producing the lowest one. Over 80% of COD was removed for all carbon sources tested. The E_c ranged from 22 to 34%. Our results indicated that all the monosaccharides in a hydrolysate

from acid hydrolysis of lignocellulosic materials could be used for electricity generation.

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