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Short communication

Effects of furan derivatives and phenolic compounds on electricity generation in microbial fuel cells

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ABSTRACT

Lignocellulosic biomass is an attractive fuel source for MFCs due to its renewable nature and ready availability. Furan derivatives and phenolic compounds could be potentially formed during the pre-treatment process of lignocellulosic biomass. In this study, voltage generation from these compounds and the effects of these compounds on voltage generation from glucose in air-cathode microbial fuel cells (MFCs) were examined. Except for 5-hydroxymethyl furfural (5-HMF), all the other compounds tested were unable to be utilized directly for electricity production in MFCs in the absence of other electron donors. One furan derivative, 5-HMF and two phenolic compounds, *trans*-cinnamic acid and 3,5-dimethoxy-4-hydroxycinnamic acid did not affect electricity generation from glucose at a concentration up to 10 mM. Four phenolic compounds, including syringaldehyde, vanillin, *trans*-4-hydroxy-3-methoxy, and 4-hydroxycinnamic acids inhibited electricity generation at concentrations above 5 mM. Other compounds, including 2-furaldehyde, benzyl alcohol and acetophenone, inhibited the electricity generation even at concentrations less than 0.2 mM. This study suggests that effective electricity generation from the hydrolysates of lignocellulosic biomass in MFCs may require the employment of the hydrolysis methods with low furan derivatives and phenolic compounds production, or the removal of some strong inhibitors prior to the MFC operation, or the improvement of bacterial tolerance against these compounds through the enrichment of new bacterial cultures or genetic modification of the bacterial strains.

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1. Introduction

Microbial fuel cells (MFCs) are devices that directly convert chemical energy to electricity through catalytic activities of microorganisms. One of the greatest advantages of MFCs over hydrogen- and methanol-fuel cells is that a diverse range of organic materials can be used as fuels [1,2]. Electricity has been generated in MFCs from various organic compounds, including carbohydrates [3–5], proteins [6] and fatty acids [7,8]. Lignocellulosic biomass is an attractive fuel source for MFCs due to its renewable nature and ready availability. Our recent study indeed demonstrated that all monosaccharides that can be directly generated from hydrolysis of lignocellulosic biomass were good sources for electricity generation in MFCs [5]. However, lignocellulosic biomass cannot be directly utilized by microorganisms in MFCs for electricity generation. In other words, lignocellulosic biomass has to be converted to monosaccharides or other low-molecular-weight compounds [9].

The most commonly used method of converting lignocellulosic biomass to monosaccharides is through a dilute-acid pre-treatment and subsequent acid- or enzymatic hydrolysis processes [10]. In addition to monosaccharides, the dilute-acid pre-treatment and the subsequent acid hydrolysis generate a number of byproducts, such as furan derivatives (2-furaldehyde and 5-hydroxymethyl-2-furaldehyde), phenolic compounds and carboxylic acids (acetic, formic, and levulinic acids) [11,12]. These byproducts negatively affect the cell membrane function, the growth, and the glycolysis of ethanol-producing yeast and bacteria [10,13–16]. However, some of these byproducts such as acetic acid are good substrates for electricity-generating microbes [7,17]. A hydrolysate from a dilute-acid pre-treatment of corn stover could even be directly used for electricity generation in MFCs [18]. However, the effects of these individual byproducts on electricity generation in a MFC are still poorly understood.

In this study, ten selected compounds that are either known byproducts in an acid pre-treatment or acid hydrolysis of lignocellulosic biomass or model compounds of those byproducts were thoroughly investigated as substrates in a MFC for electricity generation.

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2. Materials and methods

2.1. Materials

The following chemicals were purchased from Aldrich Chemical Company (Milwaukee, WI, USA) and used as received: 3,5-dimethoxy-4-hydroxycinnamic acid, 4-hydroxycinnamic acid, syringaldehyde, *trans*-4-hydroxy-3-methoxycinnamic acid, and 3,4-dimethoxybenzyl alcohol. Acetophenone, 2-furaldehyde, and 5-(hydroxymethyl) furfural were purchased from Acros Organics (Morris Plains, NJ, USA). *Trans*-cinnamic acid was obtained from Eastman (Kingsport, TN, USA) and vanillin was from J.T. Baker (Phillipsburg, NJ, USA). All other chemicals such as glucose and sodium phosphate were purchased from commercial sources. Non-wet proofing carbon cloth (type A) and wet-proofed (30%) carbon cloth (type B) were purchased from E-TEK (Somerset, NJ, USA) and used as electrodes in MFCs. A multimeter (model 2700) with a data acquisition system (Keithly Instruments Inc., Cleveland, OH, USA) was used for measuring voltage in a MFC. Electrically active bacteria that had been enriched from wastewater in Corvallis Wastewater Treatment Plant (Corvallis, OR) and used in our previous study were used in this study [5].

2.2. Microbial fuel cell construction

MFCs with an inner volume of 12 mL were constructed as reported previously [7] with a slight modification. A cylindrical MFC chamber with a length of 1.7 cm and a diameter of 3.0 cm was made of plexiglass. Non-wet proofing carbon cloth (type A) was cut into a circular disk with a diameter of 3.0 cm and was used as anode without further treatment. The cathode (a circular disk with a diameter of 3.0 cm) was prepared from the wet-proofed (30%) carbon cloth (type B) according to the procedures described previously [8]. The anode and cathode were fixed to the ends of the cylindrical chamber and connected to the circuit with titanium wire. The anode was parallel to the cathode, and the distance between the two electrodes was 1.7 cm. The anode side of the chamber was covered with a plexiglass plate while the cathode was directly exposed to air.

2.3. MFC operation with selected compounds used as sole carbon sources for electricity generation

A vitamin stock solution and a mineral stock solution were prepared according to literature procedures [17]. A glucose-free culture media solution was prepared by dissolving the following compounds in water at room temperature: $\text{NaH}_2\text{PO}_4 \cdot 7\text{H}_2\text{O}$ (15.47 g L^{-1}), $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ (5.84 g L^{-1}), NH_4Cl (0.31 g L^{-1}), KCl (0.13 g L^{-1}), a vitamin stock solution (12.5 mL L^{-1}) and a mineral stock solution (12.5 mL L^{-1}). A glucose-containing culture media was prepared separately by adding glucose (1200 mg L^{-1}) into the glucose-free culture media solution. The stock solutions of the individual furan derivatives and phenolic compounds were prepared by adding each compound in the following amount to the glucose-free culture medium (50 mL) (40 mM): 5-HMF (64 mg), syringaldehyde (45.5 mg), vanillin (38 mg), *trans*-cinnamic acid (37 mg), *trans*-4-hydroxy-3-methoxy-cinnamic acid (48.5 mg), 4-hydroxy-cinnamic acid (41 mg), 3,5-dimethoxy-4-hydroxy-cinnamic acids (56 mg). These stock solutions were diluted with the glucose-free medium solution 1 mL stock solution + 39 mL glucose-free medium to obtain 1 mM concentration of the compound and used to investigate voltage generation from these compounds in the absence of other carbon sources.

The glucose-containing culture medium solution (7.0 mL) was added into each of the MFCs, followed by a suspension of the electrically active bacteria (5 mL) that had been obtained and used for our previous study [5]. Immediately after adding the bacteria sus-

pension, MFCs were hooked up to a data acquisition system to start monitoring the voltage generation. When a stable voltage output was obtained in the MFCs, the glucose-containing culture media solution was replaced by the furan derivatives and phenolic compounds solutions. Ten MFCs were operated in a batch-fed mode simultaneously.

2.4. MFC operation to study the effects of selected compounds on electricity generation from glucose

The stock solutions of furan derivatives and phenolic compounds prepared in Section 2.3 were diluted with the glucose-free medium solution to obtain final concentrations ranged from 0.01 to 40 mM. Glucose was added to each of the diluted solutions to obtain a 1200 mg L^{-1} final concentration.

MFCs used in this set of experiments were started up following the same procedures as described in Section 2.3. When a stable voltage output was obtained, the glucose-containing medium solution was replaced by a medium solution containing both glucose and one of the furan derivatives or phenolic compounds (0.01 mM). At the end of the batch (voltage output less than 50 mV), the solution was replaced with a new medium solution containing a higher concentration of the selected compound. The concentration of the selected compound was continuously increased until a significantly reduced voltage generation was observed. The medium solution was then replaced with the glucose-containing (without selected compound) medium solution to investigate if voltage generation can be recovered.

All MFCs were operated at a fixed external resistance of 1000Ω and kept in an incubator with a constant temperature of $30 \pm 2^\circ\text{C}$ throughout the experiments.

3. Results and discussion

3.1. Voltage generation using selected compounds as the sole carbon sources

All the test compounds were selected based on their potential presence in an acid pre-treatment or acid hydrolysis of lignocellulosic biomass. These compounds were individually tested as the sole carbon source for electricity production in MFCs. A voltage of 0.46 V was produced after the solution was replaced with the 10 mM 5-HMF solution but quickly decreased to less than 0.4 V. In the subsequent batches, i.e. when the MFC solution was replaced with a fresh glucose-free medium containing the same amount of 5-HMF, the voltage decreased to 0.12 V (Fig. 1). None of the other compounds tested were able to produce electricity in the absence of the additional carbon sources (data not shown).

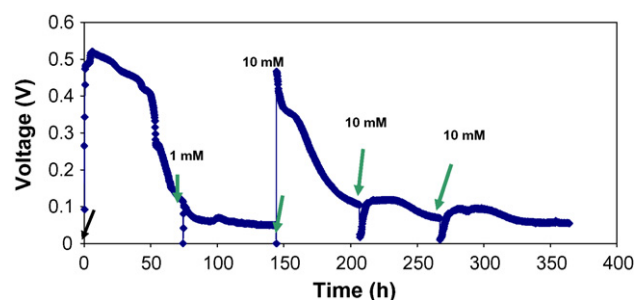


Fig. 1. Electricity generation from 5-HMF in the absence of carbon sources. Black arrow indicates the addition of glucose-containing medium and green arrows indicate the addition of 5-HMF containing medium solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

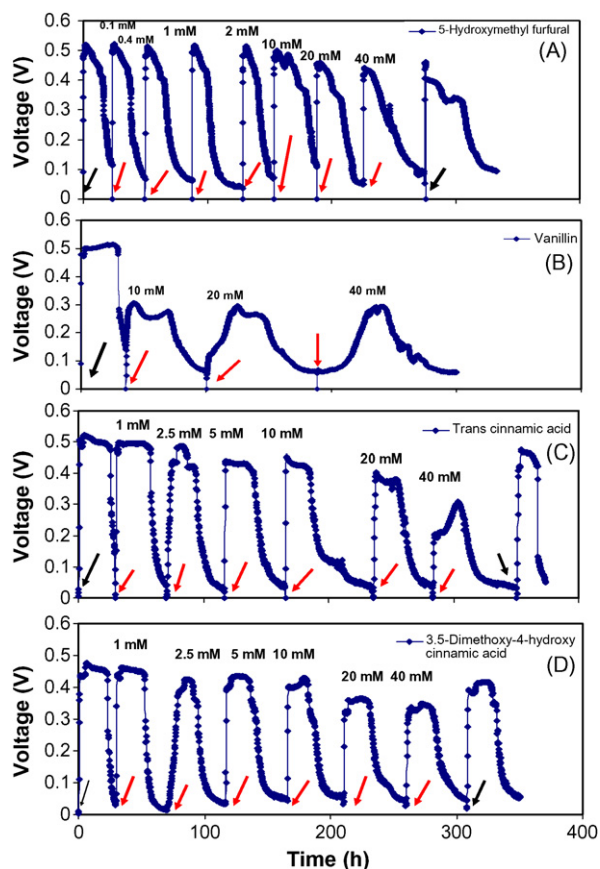


Fig. 2. Influence of 5-HMF (A), vanillin (B), *trans*-cinnamic acid (C), 3,5-dimethoxy-4-hydroxy cinnamic acid (D) on voltage generation. Black arrows indicate the addition of glucose-containing medium and red arrows indicate the addition of medium solution containing both glucose and the selected compounds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.2. Influence of 5-HMF, vanillin, *trans* cinnamic acids and 3,5-dimethoxy-4-hydroxy-cinnamic acid on voltage generation from glucose.

The maximum voltage output was not affected by 5-HMF at a concentration of up to 10 mM and decreased only about 12% when the HMF concentration was increased from 10 to 40 mM (Fig. 2A). Voltage was quickly recovered to the original level after replacing the solution with a glucose-containing medium without 5-HMF (Fig. 2A). Similar effects on voltage generation were observed for vanillin, *trans*-, and 3,5-dimethoxy-4-hydroxy-cinnamic acids except that the maximum voltage decreased about 25% for *trans*-cinnamic acid when its concentration was increased from 20 to 40 mM (Fig. 2B–D).

5-HMF is formed by dehydration of hexoses such as glucose, during the pre-treatment of biomass [19] and can inhibit ethanogenic microorganisms such as yeasts, at a concentration of ~8–120 mM (1–15 g L⁻¹) depending on the strain used [11]. The concentration of 5-HMF was generally low when steam explosion pre-treatment was applied and it ranged from 0.47 mM (0.06 g L⁻¹) to 4.7 mM (0.6 g L⁻¹) in the hydrolysates of sugar cane, corn stover and poplar [20,21]. These concentrations were much lower than 40 mM, at which the electricity generation was affected in MFCs. However, higher concentrations of 5-HMF 16–46 mM (2–5.9 g L⁻¹) were detected in the hydrolysate of spruce when one- or two-step dilute-acid hydrolysis was performed [11,22]. Cinnamic acids can also

be found in the hydrolysate of lignocellulosic biomass. It was reported that the cinnamic acid concentration was about 0.007 mM (0.001 g L⁻¹) after dilute-acid hydrolysis of spruce [16]. However, these concentrations were significantly lower than the 20 mM, at which could inhibit voltage generation in MFCs.

3.3. Influence of syringaldehydhe, *trans*-4-hydroxy-3-methoxy cinnamic acid, and 4-hydroxy cinnamic acid on voltage generation from glucose

These compounds did not affect electricity generation at lower concentrations, i.e., up to 2.5–5 mM, but severely inhibited the voltage output at higher concentrations (20 mM). At a concentration of 5 mM, syringaldehyde did not significantly affect the maximum voltage detected in comparison to that of the control. Voltage output was strongly inhibited by the addition of 20 mM syringaldehyde and reduced to 0.09 V (Fig. 3A). Similar results were observed for *trans*-4-hydroxy-3-methoxy acid (Fig. 3B). While a voltage of 0.44 V was obtained with the addition of 10 mM 4-hydroxy cinnamic acid, nearly no voltage was produced when its concentration increased to 20 mM (Fig. 3C). Voltage production was not recovered by subsequent replacement of medium solutions with fresh ones lacking these phenolic compounds (Fig. 3).

Syringaldehyde and vanillin can be formed in the degradation of syringyl propane units and guaiacylpropane units of lignin [23]. It was reported that vanillin and syringaldehyde concentrations were around 0.8 mM (0.12 g L⁻¹) and 0.6 mM (0.107 g L⁻¹), respectively in the solution after dilute-acid hydrolysis of spruce [13], 0.18 mM (0.032 g L⁻¹) and 0.16 mM (0.024 g L⁻¹), respectively after wet oxidation hydrolysis of wheat straw [16], and 0.27 mM (50 mg L⁻¹) and 0.09 mM (14 mg L⁻¹), respectively in the steam exploded poplar hydrolysates [23]. Their concentrations in poplar wood hydrolysate could be further decreased to 0.08–10 μM (0.014–1.82 mg L⁻¹)

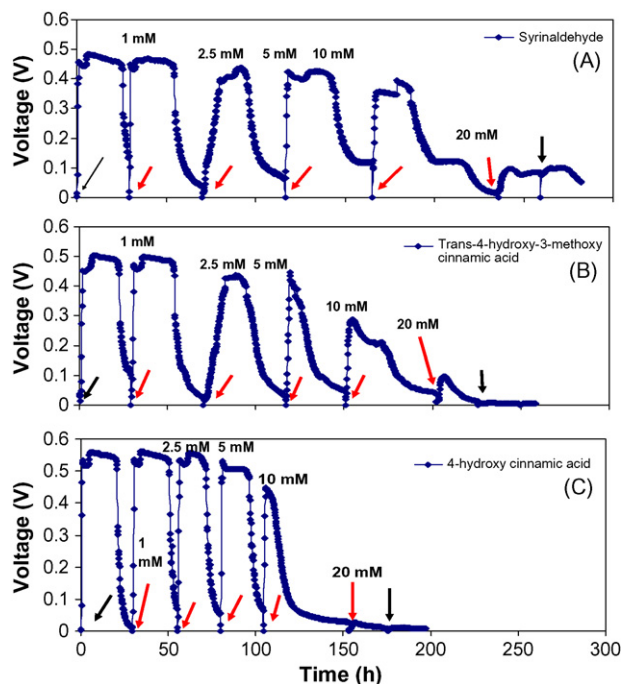


Fig. 3. Influence of syringaldehydhe (A), *trans*-4-hydroxy-3-methoxy cinnamic acid (B), and 4-hydroxy cinnamic acid (C) on voltage generation. Black arrows indicate the addition of glucose-containing medium and red arrows indicate the addition of medium solution containing both glucose and the selected compounds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

and 0.13–17 μM (0.02–2.65 mg L^{-1}), respectively using enzymatic treatment [12]. These concentrations obtained using various pre-treatment and hydrolysis methods were all much lower than the 10 mM, at which the voltage generation was inhibited, indicating that these compounds may not be a concern when the hydrolysates of lignocellulosic biomass were directly used in MFCs for power generation.

3.4. Influence of furaldehyde, acetophenone, and 3,4-dimethoxybenzyl alcohol on voltage generation from glucose

MFC performance was affected significantly by the presence of 2-furaldehyde, acetophenone, and 3,4-dimethoxybenzyl alcohol even at a concentration less than 0.1 mM. While the voltage output was not affected by the addition of 0.01 mM 2-furaldehyde, nearly 17% decrease in voltage production was observed when its concentration was increased to 0.05 mM. Following the MFC operation with 0.2 mM of 2-furaldehyde, voltage generation was not recovered upon the replacement of the medium with the glucose-containing furaldehyde-free medium solution (Fig. 4A). Acetophenone and 3,4-dimethoxybenzyl alcohol demonstrated inhibitory effects on electricity generation at 0.05 and 0.1 mM, respectively (Fig. 4B and C). Voltage generation was also not recovered using the glucose-containing medium after the MFCs were operated with 0.2 mM acetophenone and dimethoxybenzyl alcohol solutions.

Furaldehyde, a well known inhibitor for ethanologenic microorganisms, can be generated from the acid hydrolysis of hemicellulose [24]. The concentration of 2-furaldehyde can be as high as 10 mM (1 g L^{-1}) in the hydrolysate of spruce when two-stage dilute-acid hydrolysis treatment was used [25]. A lower concentration ($\sim 5.2 \text{ mM}$; 0.5 g L^{-1}) was reported when one step dilute-acid treatment was used [26]. Benzyl alcohol was also found in the

hydrolysate of steam explosion pre-treated poplar with a concentration of $\sim 6 \text{ mM}$ (0.76 g L^{-1}) [22]. The acetophenone concentration in the hydrolysate of wheat was $\sim 0.03 \text{ mM}$ (0.004 g L^{-1}) using alkaline wet oxidation method. The concentrations of these three compounds in the hydrolysates of biomass were either similar or higher than that at which inhibitory effect was observed in MFC, indicating that alternative or additional approaches should be employed to increase the efficiency of electricity generation from the hydrolysates of lignocellulosic biomass, such as: (1) use of appropriate pre-treatment methods to yield low furan derivatives and phenolic compounds production, (2) removal of some strong inhibitors prior to the MFC process [16], and (3) increasing the tolerance of bacteria towards these compounds through the enrichment of new bacterial cultures or genetic modification of the bacterial strains.

4. Conclusions

Among the 2 furan derivatives and 8 phenolic compounds tested in this study, electricity was produced only from 5-HMF with a voltage output much lower than that using glucose. All the other compounds tested were unable to directly produce electricity in MFCs in the absence of other electron donors. When glucose was used as the carbon source, electricity generation was not significantly affected by the addition of 5-HMF, *trans*-, 3,5-dimethoxy-4-hydroxy-cinnamic acids at a concentration up to 10 mM while syringaldehyde, vanillin, *trans*-4-hydroxy-3-methoxy, and 4-hydroxy cinnamic acids inhibited voltage generation at concentrations above 5 mM. Electricity generation was severely inhibited by 2-furaldehyde, acetophenone and 3-4-dimethoxybenzyl alcohol at a concentration less than 0.2 mM.

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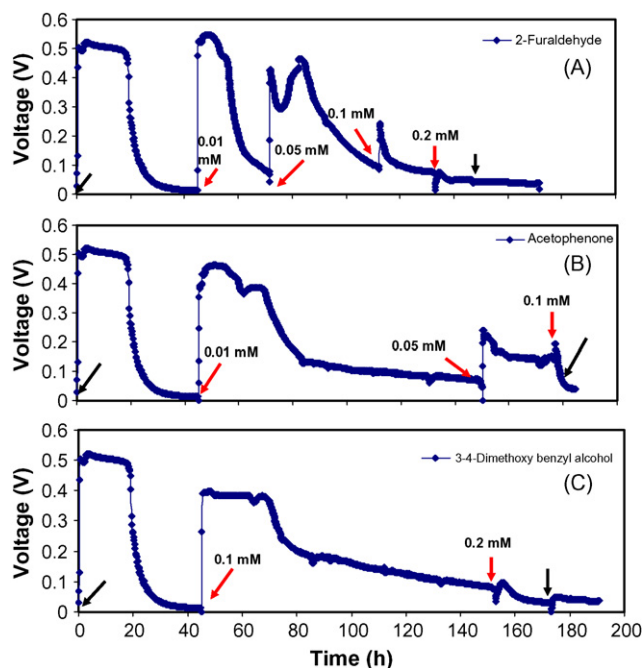


Fig. 4. Influence of furaldehyde (A), acetophenone (B), and 3,4-dimethoxybenzyl alcohol (C) on voltage generation. Black arrows indicate the addition of glucose-containing medium and red arrows indicate the addition of medium solution containing both glucose and the selected compounds. Longer operation time (45 h) for the fed-batch experiment with glucose-containing medium was used in comparison with that (25–30 h) in Figs. 2 and 3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

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