A Novel V-Shaped Microbial Fuel Cell for Electricity Generation in Biodegrading Rice Straw Compost

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***Abstract*—The study combined anaerobic composting of untreated rice straw with V-shaped microbial fuel cell (V-MFC) to investigate the hydrolysis of lignocellulose and electricity generation of V-MFC. Due to the configuration for V-MFC, protons that be generated by the process of lignocellulose degradation could be accumulated with composting liquid at the bottom of V-MFC, and increased the contact area between polyvinyl alcohol-membrane electrode assembly (PVA-MEA) and rice straw compost. Therefore, V-MFC can buffer the variation of proton concentration in anode chamber and also improve the problem of unstable voltage output caused by environmental temperature. Experimental results show that lignocellulose material used in fed-batch MFC can operate up to 120 days until the liquid in system was consumed. V-MFC can consistently generate stable voltage of 277±10 mV for 75 days, the maximum voltage output of 307 mV, the maximum power density of 112mW/m^3 with the internal resistance of 607 Ω. The experiments demonstrate that the process lignocellulose decomposing bacteria (LDB) degraded lignocellulose can generate power. Thus, this method provides a promising way to utilize compositing of rice straw for bioenergy production.**

***Index Terms*—V-shaped microbial fuel cell (V-MFC), lignocellulose, rice straw, proton, polyvinyl alcohol-membrane electrode assembly (PVA-MEA), bioelectricity generation.**

I. Introduction

Rice is one of the main agricultural products in Taiwan. After harvesting, There are about 2 million tons of rice straws produced per year [1]. Rice straw a common agricultural lignocellulosic wastes is a mixture of cellulose, hemicellulose, lignin and minor amounts of other organics [2]. But most of waste rice straw was not efficiently utilized or recycled due to its bulkiness, high volume and low price; therefore, lots of farmers choose to bury or burn rice straw as disposal method. As a result, this disposal method causes waste of resources and emission of air pollutants [3].

Microbial fuel cell (MFC) has been under development for decades and a wide range of substrates has been explored as fuel [4]. Early MFC studies mostly used acetate [5], glucose [6], or other simple substrates as fuel [7]. A combination of MFC and wastewater treatment has been widely discussed in recent years, such as domestic wastewater [8], olive mill wastewater [9], swine wastewater [10] and brewery wastewater [11]. Nowadays, the utilization of solid organic waste in MFC has been gradually developed [12], [13]. However, solid phase microbial fuel cell (SMFC) can generate electricity with solid organic waste such as sludge, sediment and contaminated soil [14]. A practical application of SMFC faces the challenges of limited output power and short sustained discharge time, as well as low mass transfer rate in the anode chamber. The efficacy of power output can be increased with the addition of organic materials, such as plant rhizodeposits or biomass like chitin or cellulose.

Solid organic wastes rich in organic matter have been considered as a potential fuel source of MFC, but the application of SMFC are usually affected by system configuration [15]. The configuration of MFC will cause mass transfer limitation and uneven fuel distribution in anode chamber that result in higher internal resistance and lower power output [12]. However, for single-chamber air cathode MFC, several researchers have reported that the effect of ambient temperature

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variation on air cathode is a key factor of electricity generation [16], [17]. Furthermore, Wei [18] explored the effect of environmental temperature on MFC performance and pointed out that temperature can influence microbial activity and cause the variation of proton concentration in single-chamber air cathode MFC; thus, the trend of voltage generation was unstable.

Although several MFC studies have been developed on the utilization of cellulolysis lignocellulose [19]-[22], use untreated lignocellulosic wastes as fuel in MFC is rarely [23]; therefore, the compost made from rice straw after harvest and commercial bioorganic fertilizer was used as fuel in this study. For lignocellulosic materials in composting processes, most of composting is a managed aerobic microbial process that breaks down lignocellulosic wastes into compost [24]. But the anode of the MFC has to maintain an anaerobic environment to avoid oxygen intrusion to anode chamber. To solve the conflicting problem that utilize lignocellulose composition to generate energy, this study used the self-designed V-shaped MFC system to increase the contact area between fuel and PVA-MEA, promote the application of lignocellulose in MFC and improve the problem of unstable voltage output for single chamber MFC. Furthermore, the upper space of V-MFC is dry and aerobic (conducive to the degradation of rice straw), the lower space of V-MFC is anaerobic due to accumulation of composting liquid (conducive to anodic microbial metabolism in electricity). Moreover, the bottom of V-MFC formed a groove so that V-MFC could buffer the variation in proton concentration of microbial metabolism, thereby expanding the decomposition of rice straw and energy efficiency in MFC.

II. Materials and Methods

A. MFC Construction and Operation

The architecture of the chamber for the experiment is shown in Fig. 1. V-shaped MFC was constructed of acrylic plates, volume of 950 mL, the air cathodes (7 cm × 7 cm) attached to both sides of chamber [25] and carbon felt (7 cm × 7 cm, C0S3003, Phychemi, Chain) was used as anode. The anode was pretreated by heating at 80 °C for 1 h in 15% nitric acid solution to remove organic matters before use [26]. Two holes were drilled into the top surface of chamber for sample extraction and electrode connection, anode and air-cathodes were connected to titanium wire (0.4 mm) and a 1kΩ external resistor in a loop. Air-cathodes were prepared using 9% polyvinyl alcohol (BF-26, Chang Chun Petrochemical Co., Ltd, Taiwan) and carbon cloth (0.7 mm thickness, CW1001, KoTHmex, Taiwan) by freezing-thawing process and cross-linked physically with polymer crystallites acting as network junction points [27], [28] to render PVA films flexible and water insoluble.

B. Rice Straw Compost

This study used commercial organic fertilizer (Dragon of the 6th Enzyme Organic Fertilizer, Fang Yuan Biochemical Technology Co., Ltd.) as bacterial strains, and the organic fertilizer includes rice bran, carbonized rice husks, mushroom cultivation materials, eggs and effective microorganisms including *Actinobacteria*, *Morchella* spp., yeast, *Trichoderma harzianum* and *bacillus subtilis*) and the N-P-K content of 4% , 2.5% and 2.5%, respectively. Waste rice straw was harvested from rice farm in Changhua County, Taiwan and dry up the straw in the sun for 5–7 days. Rice straw is difficult to be degraded because of its complex, lignocellulosic structure, for this reason rice straw was cut into smaller pieces of length 4–5 cm and soaked in water for 2–3 days before composting. Phosphate buffer solution was added to rice straw compost to ensure the environment was suitable for bacterial growth. Each liter of phosphate buffer solution contained K_2HPO_4 1750 mg, KH_2PO_4 2145 mg, NH_4Cl 10 mg, $MgCl_2 \cdot 6H_2O$ 1000 mg, $CaCl_2 \cdot 2H_2O$ 45 mg, $CuCl_2 \cdot 2H_2O$ 0.25 mg, $CoCl_2 \cdot 6H_2O$ 0.25 mg, $ZnCl_2$ 1.0 mg, $MnCl_2 \cdot 4H_2O$ 1.0 mg, $Na_2MoO_4 \cdot 2H_2O$ 0.1 mg and $NiCl_2 \cdot 6H_2O$ 0.02 mg.

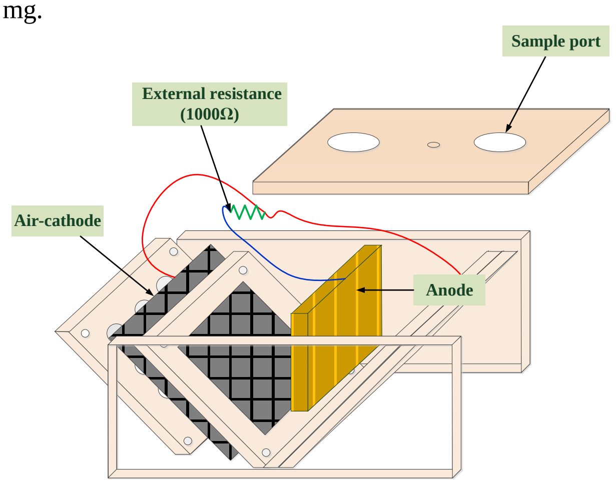

Figure 1. Schematic diagram for V-shaped MFC

C. Electrochemical Analysis and Calculations

Voltage was measured every 2 min using a digital multimeter (Integra 2700 series equipped with 7700 multiplexer, Keithley Instruments, Inc., Cleveland, U.S.A.) interfaced to a personal computer. The polarization curves and the power density curves were obtained by varying the external resistance from 500k Ω to 50 Ω during stabilized MFC operation every 10 min after each resistance load was changed. Internal resistance was calculated by linear regression of voltage vs. current and open circuit voltage was the voltage obtained at zero current.

D. Fibre Analysis

The fibre concentration of rice straw compost used the Neutral Detergent Fibre (NDF), Acid Detergent Fibre (ADF) and Acid Digestible Lignin (ADL) tests [29]. In the NDF test, the sample is boiled with neutral detergents (ND) with a pH of 7.0. The degradable materials are removed (sugars, starch, pectins and fats), and the insoluble NDF fraction remains. The NDF contains cellulose, hemicellulose, lignin, silica, and any heat-damaged protein. In the ADF test, the sample is boiled with acid detergents (AD). The cell content and hemicellulose are removed, and the insoluble ADF fraction remains. The ADF contains cellulose and lignin. In the ADL test, the ADF residue is extracted with 72% H_2SO_4, and the ADL fraction is obtained. The ADL contains lignin and mineral ash. Conclusively, hemicellulose was calculated as NDF substracted by ADF, cellulose as ADF substracted by ADL and lignin was directly determined by the results of ADL [30].

E. Reducing Sugar Concentration Analysis

The reducing sugars liberated were estimated by DNS method [31]. DNS method is based on reduction of 3,5-dinitrosalicylic acid (DNS) reagent with reducing sugars to produce an reddish-brown colored 3-amino-5-nitrosalicylic acid solution which measured using UV spectrometer at 550 nm. The sample was calculated by comparison with the standard curve of glucose [32].

III. Results and Discussion

A. Sugar Yield and Fibre Composition Under Open-Circuit / Closed-Circuit Condition

To prove MFC can increase the degradation rate of rice straw and clarify the relationship between metabolic products and electricity generation, this study operated MFC system under open and closed circuit conditions. Also, reducing sugar content (Fig. 2a) and fibre composition (Fig. 2b) after the operation were measured. Because lignocellulosic materials in rice straw can be hydrolyzed to simple soluble sugars, and others were converted to volatile fatty acids, Fig. 2a shows the concentration profiles of reducing sugar during compositing of rice straw degradation throughout the bioelectricity generation process. Compared the variation in reducing sugar content in open and closed circuit conditions: during the initial period of the system operation (0–9 days), open circuit condition containing 569 ppm of reducing sugar and closed circuit condition containing 610 ppm of reducing sugar, the difference of reducing sugar content between open and closed circuit was small; from 10 days to end of the operation period, the experimental result shows the reducing sugar concentration of open circuit condition was continuously higher than closed circuit condition, indicated that the sugar materials were accumulated at open circuit condition and the rate of sugar utilization also lower than closed circuit condition. A similar result was also reported that the MFC was operated initially on lignocellulosic wastes had lower cellulose degradation rate and sugar yield; but with the cellulose was hydrolyzed to sugars gradually, the reducing sugar concentration reached maximum and decreased by microbial degradation of sugar [31], [32].

According to research by Saha et al. [33], rice straw predominantly contains cellulose 32–47%, hemicelluloses 19–27% and lignin 5–24%, and ashes 18.8%. Rice straw in this study contains cellulose 52.25%, hemicellulose 15.41%, lignin 6.33%, ashes and others 26.01%. Fig. 2b shows the effect of power generation on fibre composition of rice straw after 30 days of V-MFC operation. Under open-circuit condition (no current generation), rice straw contains cellulose 40.27%, hemicellulose 15.72%, lignin 5.23%, ashes and others 38.78%. Under closed-circuit condition (with current generation), rice straw contains cellulose 36.28%, hemicellulose 18.21%, lignin 3.59%, ashes and others 41.92%. Compared with lignocellulose degradation of open-circuit condition, lignocellulose degradation of closed-circuit condition was 3.14% higher than open-circuit. Previous researches had shown that using MFC to treat organic pollutant could improve the organic matter removal and the organic removal rate of closed-circuit condition would higher than open-circuit condition. Different substrates as fuel such as synthetic wastewater [34], sodium acetate synthetic wastewater [35] and Luria Bertani broth (LDB) [36] operated under open and closed circuit condition were reported, and also shown difference in COD removal efficiency (about 3.5%–26%) between open and closed circuit condition. These results show that the current-generating anode in MFC could provide sufficient organic removal efficiency.

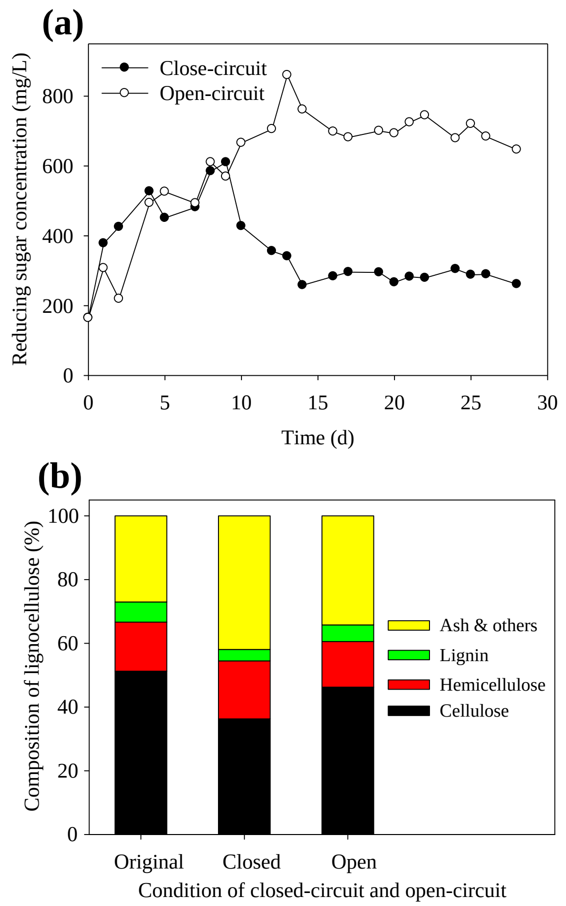

Figure 2. Reducing sugar (a) and rice straw (b) content variations under open/closed conditions.

B. Electricity Production in V-MFC

V-MFC was operated at room temperature by adding 200 g drying rice straw, 40 g organic fertilizer and 800 mL phosphate buffer solution as fuel. The novel construction of V-MFC caused the bottom of anode chamber formed a groove, which could store up the liquid generated from the compost process and make protons accumulated at the bottom of anode chamber. Consequently, V-MFC had a buffer region to accumulate or release protons and mitigated the effect of temperature on the variation of proton concentration in anode chamber. Fig. 3 presents the generation of voltage in V-MFC. The average voltage was 277 ±10 mV and stable voltage output of 75 days during the first period. In the second period (76–105 days), because the inhibition of proton transfer produced by a low water content, which was resulted from evapotranspiration [16], [37], the average voltage decreased to 200 mV and the voltage amplitude reached 95 mV. According to the preliminary report, the initial lag phase appeared at the initial incubation, and then it disappeared after successive transfers of new media, suggesting that electricity generation from rice straw was primarily due to direct electron transfer by cellulose-degrading bacteria (CDB) attached to the anode and did not require accumulation of mediators in the fresh solution [31]. This longer stable period for power generation might have been due to the different composition of lignocellulosic substrates of rice straw. The electricity can be produced from a wheat straw hydrolysate as the substrate in an MFC with a long stable period of power generation.

To prove the effect of the groove in V-MFC on voltage change, V-MFC operated under the same condition, but the groove was filled by expandable polystyrene. The trend of voltage generation in groove-filled V-MFC is shown in Fig. 4a. The voltage amplitude is increased in groove-filled V-MFC, and normal V-MFC maintains a stable voltage output. This result shows that the novel configuration for V-MFC makes protons be stored at the bottom groove of anode chamber and improves the effect of temperature on unstable voltage output. As shown in Fig, 4b, V-MFC displays maximum power density of 112.0 mW/m^3 under current density of 407.4 mA/m^3 with the internal resistance of 607 Ω.

On the other hand, another V-MFC was operated at different temperature-controlled conditions to investigate the variation of pH between top and bottom of V-MFC. V-MFC operations were conducted at temperatures of 18 ^{o}C, 35 ^{o}C and room temperature for 3 hours and measured pH values in liquid surface and groove of V-MFC. As shown in Table I, the differences of pH in liquid surface under different temperatures were small, the pH values at different temperatures were maintained at 7. But the pH in groove was increased from 6.73 to 6.95 during V-MFC operated at 18 ^{o}C and decreased from 6.73 to 6.51 during V-MFC operated at 35 ^{o}C. These results suggest that due to the effect of temperature on microbial activity [38], the protons of anode chamber were utilized at low temperature and accumulated at high temperature.

C. Fibre Composition Analysis

In this experiment, rice straw that had been operated in V-MFC for 30 days was tested. As shown in Fig. 5, the composition of rice straw collected at top of reactor was 32.84% cellulose, 23.76% hemicellulose, 3.17% lignin, and 40.23% ashes and others；the rice straw collected at bottom of reactor contained 46.24% cellulose, 14.31% hemicellulose, 5.23% lignin, and 34.22% ashes and others. There is some evidence to suggest that the upper space of V-MFC is dry aerobic condition and conducive to the degradation of rice straw; the lower space of V-MFC is anaerobic condition which due to accumulation of liquids and lignocellulose degradation is slow. Accordingly, the lignocellulose removal efficiency of upper space of V-MFC is better than lower space of V-MFC and indirectly proving that the difference between top and bottom of V-MFC is suitable for application of solid compost in MFC system.

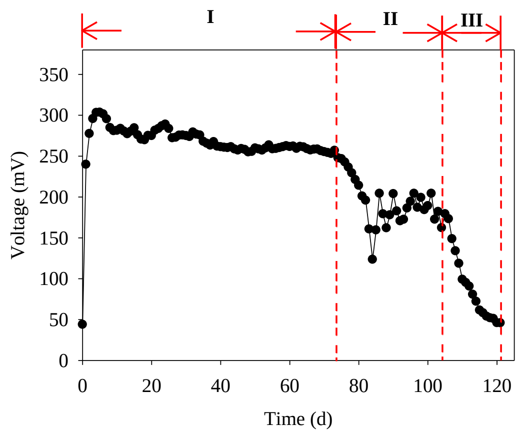

Figure 3. Generation of voltage in V-MFC.

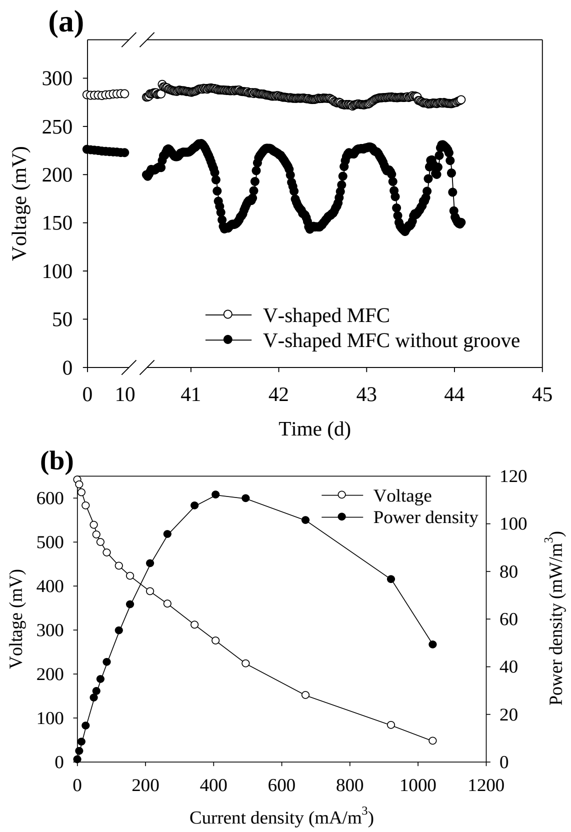

Figure 4. Trend of electricity generation (a) and power density curve (b).

Figure 5. Composition of rice straw at various sampling locations.

TABLE I. PH VARIATIONS UNDER VARIOUS TEMPERATURES IN V-MFC.

Temperature (°C)	pH at various sampling locations	
	Top	Bottom
Room	7.02	6.73
18	7.01	6.95
35	6.95	6.51

IV. CONCLUSIONS

According to the results of V-MFC under open and closed circuit conditions, rice straw used in MFC could speed up the composting process and increase the utilization of rice straw. This study included the development of the V-shaped MFC system and promoted the durability of electricity generation from MFC and provided over 75 days of the voltage output. Furthermore, due to the novel configuration for V-MFC making protons being stored at the bottom reservoir of reactor, V-MFC improved the problem of unstable voltage output on single chamber MFC caused by ambient temperature and enhanced the feasibility of MFC technologies for real-world application.

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