WHOLE SYSTEMS THINKING FOR SUSTAINABLE WATER TREATMENT DESIGN

by

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Whole Systems Thinking for Sustainable Water Treatment Design
Thesis directed by Assistant Professor Zhiyong Ren

**ABSTRACT**

Microbial fuel cell (MFC) technology could provide a low cost alternative to conventional aerated wastewater treatment, however there has been little comparison between MFC and aeration treatment using real wastewater substrate. This study attempts to directly compare the wastewater treatment efficiency and energy consumption and generation among three reactor systems, a traditional aeration process, a simple submerged MFC configuration, and a control reactor acting similar as natural lagoons. Results showed that all three systems were able to remove >90% of COD, but the aeration used shorter time (8 days) then the MFC (10 days) and control reactor (25 days). Compared to aeration, the MFC showed lower removal efficiency in high COD concentration but much higher efficiency when the COD is low. Only the aeration system showed complete nitrification during the operation, reflected by completed ammonia removal and nitrate accumulation. Suspended solid measurements showed that MFC reduced sludge production by 52-82% as compared to aeration, and it also saved 100% of aeration energy. Furthermore, though not designed for high power generation, the MFC reactor showed a 0.3 Wh/g COD/L or 24 Wh/m³ (wastewater treated) net energy gain in electricity generation. These results demonstrate that MFC technology could be integrated into wastewater infrastructure to meet effluent quality and save operational cost.
The high cost and life-cycle impact of electrode materials is one major barrier to the large scale application of microbial fuel cells (MFC). We also demonstrate that biomass-derived black carbon (biochar), could be a more cost effective and sustainable alternative to granular activated carbon (GAC) and graphite granule (GG) electrodes. In a comparison study, two biochar materials made from lodgepole pine sawdust pellets (BCp) and lodgepole pine woodchips (BCc), gassified at a highest heat temperature (HHT) of 1000°C under a heating rate of 16°C/min, showed a satisfactory power density of 532 ± 18 mW m\(^{-2}\) and 457 ± 20 mW/m\(^{-2}\) respectively, compared to GAC with 674 ± 10 mW m\(^{-2}\) and GG with 566 ± 5 mW m-2 (normalized to cathode projected surface area), as an anode material in a two-chamber MFC. BCc and BCp had BET-N2 surface area measurements of 429 cm\(^2\) g\(^{-1}\) and 470 cm\(^2\) g\(^{-1}\) respectively, lower than industrial GAC with 1248 cm\(^2\) g\(^{-1}\) but several orders of magnitude higher than GG with 0.44 cm\(^2\) g\(^{-1}\). BCc and BCp had a lower surface resistance of 3±1Ω mm\(^{-1}\) and 6±1 Ω mm\(^{-1}\) than 8±2Ω mm\(^{-1}\) for GAC, but higher that GG with 0.4±0.5 Ω mm\(^{-1}\). We also investigated the life-cycle impact and estimated cost of biochar as an electrode material. Although there is no well-established market price for biochar, conservative estimates place the costs around 51-356 US$/tonne, up to ten times cheaper that GAC (500-2500 US$/tonne) and GGs (500-800 US$/tonne) with significantly greater life-cycle advantages.

The form and content of this abstract are approved. I recommend its publication.

Approved: Zhiyong Ren
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CHAPTER I

INTRODUCTION

The current global wastewater infrastructure system has several major limitations. In the developed world the wastewater infrastructure provides for adequate treatment, but can be extremely expensive and energy intensive. In the developing world there is a serious lack of wastewater infrastructure, which can lead to pollution and the spread of infectious diseases. In both cases the wastewater stream is treated as a separate system and does not generally tie into other civil processes. This thesis is an attempt to use microbial fuel cell technology and biochar electrodes to lower the cost, decrease energy use, and integrate wastewater treatment into agricultural production and land reclamation.
CHAPTER II

ENERGY AND PERFORMANCE COMPARISON OF MICROBIAL FUEL CELL AND CONVENTIONAL AERATION TREATMENT OF INDUSTRIAL WASTEWATER

Abstract

Microbial fuel cell (MFC) technology could provide a low cost alternative to conventional aerated wastewater treatment, however there has been little comparison between MFC and aeration treatment using real wastewater substrate. This study attempts to directly compare the wastewater treatment efficiency and energy consumption and generation among three reactor systems, a traditional aeration process, a simple submerged MFC configuration, and a control reactor acting similar as natural lagoons. Results showed that all three systems were able to remove >90% of COD, but the aeration used shorter time (8 days) than the MFC (10 days) and control reactor (25 days). Compared to aeration, the MFC showed lower removal efficiency in high COD concentration but much higher efficiency when the COD is low. Only the aeration system showed complete nitrification during the operation, reflected by completed ammonia removal and nitrate accumulation. Suspended solid measurements showed that MFC reduced sludge production by 52-82% as compared to aeration, and it also saved 100% of aeration energy. Furthermore, though not designed for high power generation, the MFC reactor showed a 0.3 Wh/g COD/L or 24 Wh/m³ (wastewater treated) net energy gain in electricity generation. These results demonstrate that MFC technology could be integrated into wastewater infrastructure to meet effluent quality and save operational cost.
Introduction

Traditional activated sludge or aerated lagoon wastewater treatment processes can efficiently remove organic pollutants, but operating such systems are cost and energy intensive, mainly due to the aeration and sludge treatment associated processes. The United States spends approximately $25 billion annually on domestic wastewater treatment and another $202 billion is needed for improving publicly owned treatment works. Wastewater treatment accounts for about 3% of the U.S. electrical energy load, which is approximately 110 Terawatt hours per year, or equivalent to 9.6 million households’ annual electricity use. Traditional activated sludge based treatment processes employ aerobic heterotrophic microorganisms to degrade organic matters. Such types of microbes have high metabolic kinetics, so they can process substrates faster than anaerobic bacteria, but they also require sufficient supply of oxygen and generate significant amount biomass. Aeration can amount to 45-75% of wastewater treatment plant (WWTP) energy costs, while the treatment and disposal of sludge may count up to 60% of the total operation cost.

The next generation of wastewater infrastructure should consider transforming current energy-intensive, treatment-focused processes into integrated systems that recover energy and other resources. It was estimated that the energy content embedded in wastewater is estimated about 2-4 times the energy used for its treatment, so it is possible to make wastewater treatment self-sufficient, if new technologies can recover the energy while simultaneously achieving treatment objectives. Microbial fuel cells (MFCs) recently emerged as a novel technology to fulfill this mission because they directly convert biodegradable materials into renewable energy with minimal sludge production.
MFCs employ exoelectrogenic bacteria to extract electrons from (in)organic substrates and transfer them to the anode, and the electrons then form electric currents when flowing from the anode to the cathode, where they then combine with oxygen and protons to produce water. MFCs have been shown effective in treating almost all kinds of waste streams, including municipal, brewery, agricultural, refinery, paper cycling wastewater, and even landfill leachate. The power output is dependent on the biodegradability of the substrate, conversion efficiency, and loading rate. For example, 261 mW/m² was obtained using swine wastewater while other studies have demonstrated that a maximum power output of 205 mW/m² can be achieved using brewery wastewater and 672 mWm² using paper recycling wastewater.

The functional bacteria in MFCs are generally anaerobic or facultative microorganisms, so the operation of MFCs may not use any active aeration. In addition, the cell yield of exoelectrogenic bacteria (0.07-0.16 gVSS/gCOD) was much less than the activated sludge (0.35-0.45 0.16 gVSS/gCOD), so sludge production can be significantly reduced. However, most studies have focused on energy production from MFCs while very few compared the energy use/generation and sludge production between MFCs and traditional aeration based processes. In this study, we used liter-scale reactors to quantitatively audit the power generated or consumed during the operation of an MFC, an aeration tank, and a control reactor during the treatment of wastewater. We also compared system performance in terms of COD and ammonia removal, and the concentration changes in nitrate, suspended solids, and dissolved oxygen. We aim to provide side-by-side quantitative information in evaluating the potential energy and
treatment benefits of MFCs as compared to traditional aeration processes such as activated sludge or aerated lagoon systems.

Figure I. Reactor configurations
Materials and Methods

Reactor Configuration and Construction

Three reactors including an MFC, an aeration reactor, and a control reactor, were constructed using a 15 L container. The single-chamber submerged MFC reactor was configured using graphite brush as the anode (Chemviron Carbon) and carbon cloth (1% Pt) as the air-cathode (Fuel Cell Earth LLC) (Figure I). The same 15 L container was used for the aeration reactor, with an aquarium pump air diffuser at the bottom (Figure I). The control reactor used a same type of container but without any aeration equipment or electrode installed (Figure I). All reactors were operated in fed-batch mode at room temperature and exposed to the ambient air.

Reactor Start-up and Operation

Industrial wastewater was collected from the effluent of the primary clarifier from the Coors Wastewater Treatment Plant in Golden, Colorado. The wastewater was used as the inoculum and sole substrate for all three reactors. No extra medium or buffer solution was added. The MFC reactor went through an initial 7 day inoculation period before the wastewater was replaced and measurements taken. All reactors were operated until >90% COD reduction was achieved then the wastewater was replaced for a series of three trials.

Analyses and Calculations

Closed circuit voltage (V) and amps (A) were measured and recorded using a data acquisition system (Keithley Instruments, Inc. OH) across an external resistance (R) of 10
Ω in a time interval of 3 minutes. Power in watts (W) was calculated from the equation $W = V \cdot A$. Power generation or consumption was measured during a specific time measured in hours (h), expressed in watt hours (Wh) and calculated using the equation $Wh = W \cdot h$. The wattage for the aeration pump was determined from the manufacturer’s specification, while the wattage generated from the MFC was determined from the data acquisition system and the equation described above. Polarization curve was normalized by cathode surface area and was determined by conducting a linear sweep voltammetry test using a potentiostat (G 300, Gamry Instruments). Dissolved oxygen concentration was measured with a standard DO probe (DO50-GS, Hach Co.) COD, DCOD, NH$_4^+$-N, and NO$_3^-$ concentrations were measured with digester vials (Hach Co.) according to APHA standards. The solid retention time (SRT) was calculated based on the amount of time in days (d) each reactor was operated.

**Results and Discussion**

**Organic Removal**

All three reactors were fed with the same wastewater with a COD concentration of 1247±63.9 mg/L. The reactors were operated in batch mode till reaching >90% of COD removal. While all reactors were able reach the same treatment goal, the average retention time for achieving similar treatment efficiency varied significantly (Figure II). The MFC reactor took 15 days to reach to 90% removal, which is 10 days shorter than the control reactor without aeration but 2 days longer than the aeration reactor. The shorter retention time for the aeration reactor is similar to the extended aeration activated sludge systems and can be attributed to the readily available oxygen supply and rapid metabolisms of aerobic respiration $^{10}$. The SRT of the control is around 25 days, close to
traditional stabilization lagoons, which do not employ mechanical aeration and may create aerobic, anoxic, and anaerobic layers of environment for different microbial community and metabolisms. The absence of mechanical aeration in the MFC reactor also provided an anoxic environment but experienced much shorter retention time than the control. These results suggest that by providing a submerged anode and a floating cathode, the MFC configuration significantly facilitated substrate oxidation rate close to aeration operation but without any external oxygen supply.

![Graph showing COD removal efficiency](image)

**Figure II. Comparison of COD removal efficiency between MFC, aeration, and control reactors**

Such variations can also be presented by COD removal rates. As shown in Figure III, the COD removal rates from the three systems varied significantly and changed depending on the COD concentrations. During the initial stage of operation, when the COD concentration was high, COD removal rate for the aeration reactor averaged around 12.1 mg/L·h, which was 3.6 times and 9.7 times higher than that of the MFC or control reactor treating the similar COD concentrations. However, when the COD concentration...
decreased to around 200 mg/L or less, the removal rate for the aeration reactor decreased to 0.6 mg/L·h. This rate was similar to that of the control but significantly less than that of the MFC reactor, which had an average COD reduction rate of 2.0 mg/L·h. This observation may be interpreted using the different degradation natures between suspended growth systems and attached growth systems. Many studies and models showed that compared to attached growth systems, such as trickling filters, completely mixed suspended growth systems such as activate sludge were able to treat high concentrated organics more efficiently but the effluent COD was highly depending on the solid retention time $^{10}$.

**Figure III. COD removal rates and COD removal rates at COD concentrations > 200 mg/L**

Ammonia and Nitrate Removal Efficiencies

Because the same wastewater was used as the influent for all three reactors, all systems were fed with the same ammonia concentration of 10 mg/L. However, because the aeration reactor provided a completely aerobic environment for nitrification, it showed nearly 100% ammonia removal within 11 days, after an initial concentration increase due to organic ammonification (Figure IV). This nitrification process is also confirmed by the accumulation of nitrate in the aeration reactor, where the increase of
nitrate concentration from 2 mg/L to 12 mg/L perfectly accompanied the ammonia decrease (Figure IV). No denitrification was observed in the aeration reactor due to the highly aerobic environment. In contrast, neither MFC or control reactor showed significant ammonia removal or nitrate accumulation during the operation, presumably due to inhibition of nitrification in the anoxic to anaerobic condition in such reactors. However, other studies have shown that MFC, supplemented with nitrate, experienced 94.1 ± 0.9% nitrogen removal. Our MFC reactor did show a slight nitrification process after 14 days of operation, as shown in Figure 3A-B, but we had to change the solution at the time because the reactor had reached the 90% organic removal threshold.

![Figure IV. Ammonia and nitrate removal comparison between the MFC, aeration, and control reactors.](image)

**Solids Production**

Preliminary characterization on total suspended solid (TSS) at different solid retention time shows that the aeration reactor produced much more solids than the other two reactors. The final TSS concentration from the aeration reactor was 202 ± 50 mg/L in the reactor at the corresponding SRT of 13 days. By comparison, the MFC reactor maintained the lowest TSS concentration, with 20 ± 10 mg/L, and the control reactor had
a TSS of 45 ± 10 mg/L. The low TSS concentration in the MFC reactor can be attributed to two reasons. First, the MFC is a biofilm based system, and the accumulation of biomass mainly resides on the electrode except of occasional biofilm falloff, so the suspended solid is low. Another reason is due to the low cell yield of the anoxic to anaerobic microorganisms in the MFC compared to the activated sludge. This finding confirms that sludge reduction can be a main benefit of MFC to replace activated sludge and reduce plant operation cost by 20-30%. When converting aeration basin into an MFC system, second clarifiers may be reduced in size, converted to solid contact basin, or even eliminated due to the reduced biomass generation.

MFC Electricity Production Using Wastewater as the Substrate

The MFC reactor was operated under a 10 Ω external resistance during operation. Low resistance was used in this study because under this condition more electrons can be transferred freely and substrate degradation can be maximized. The MFC generated a maximum output voltage of 135 mV and a current density of 193 mA/m². The total MFC power output during a 15-day SRT was 0.36 Wh, equivalent to 0.32 Wh/g COD/L, or 24
Wh per cubic meter wastewater treated. With an average SRT of 13 days, the aeration reactor consumed approximately 624 Wh of electricity, which transfers to about 547 Wh/g COD/L. The aeration pump could have been more efficient and adjusted to aerate less during lower levels of COD, however it was maintained as the same level in order to allow for complete nitrification and ensure oxygen was not the limiting factor.

Figure 6 shows a comparison between power consumption in the aeration reactor and energy saving and production in the MFC reactor. Though this MFC was mainly designed for COD removal not for high power production, it still saves 100% of the aeration energy and produce extra energy while achieving the same treatment goal. Due to the high energy consumption of aeration in this study, it is not representative to directly calculate how much percentage of extra energy can be produced from MFC, but based on many other studies, MFC may produce 10% of extra electricity on top of aeration energy savings, if the aeration energy consumption is assumed as 1 kWh/kg-COD\textsuperscript{12}.

![Figure VI. Power analysis for the MFC and aeration reactors.](image-url)
Conclusion

The results in this study showed that microbial fuel cell can be a viable technology to treat wastewater at the same level as traditional aeration process does, and it carries great potential as an energy positive process, because it saves 100% of aeration energy with extra electricity output. It also significantly reduces sludge production, which may reduce the size of secondary clarifier and save the cost of sludge disposal.
CHAPTER III

BIOCHAR AS A SUSTAINABLE ELECTRODE MATERIAL IN MICROBIAL FUEL CELLS

Abstract

The high cost and life-cycle impact of electrode materials is one major barrier to the large scale application of microbial fuel cells (MFC). We demonstrate that biomass-derived black carbon (biochar), could be a more cost effective and sustainable alternative to granular activated carbon (GAC) and graphite granule (GG) electrodes. In a comparison study, two biochar materials made from lodgepole pine sawdust pellets (BCp) and lodgepole pine woodchips (BCc), gassified at a highest heat temperature (HHT) of 1000°C under a heating rate of 16°C/min, showed a satisfactory power density of 532 ± 18 mW m-2 and 457 ± 20 mW/m-2 respectively, compared to GAC with 674 ± 10 mW m-2 and GG with 566 ± 5 mW m-2 (normalized to cathode projected surface area), as an anode material in a two-chamber MFC. BCc and BCp had BET-N2 surface area measurements of 429 cm2 g-1 and 470 cm2 g-1 respectively, lower than industrial GAC with 1248 cm2 g-1 but several orders of magnitude higher that GG with 0.44 cm2 g-1. BCc and BCp had a lower surface resistance of 3±1Ω mm-1 and 6±1 Ω mm-1 than 8±2Ω mm-1 for GAC, but higher that GG with 0.4±0.5 Ω mm-1. We also investigated the life-cycle impact and estimated cost of biochar as an electrode material. Although there is no well-established market price for biochar, conservative estimates place the costs around 51-356 US$/tonne, up to ten times cheaper that GAC (500-2500 US$/tonne) and GGs (500-800 US$/tonne) with significantly greater life-cycle advantages.
Introduction

Microbial fuel cell (MFC) is a new platform technology that can simultaneously achieve (in)organic biodegradation and electricity generation\textsuperscript{14–16}. MFC reactors utilize the metabolic activity of exoelectrogenic bacteria to catalyze redox reactions on the anode and promote the flow of electrons from anode to cathode for direct current harvesting\textsuperscript{12}. Compared to current energy and cost intensive wastewater treatment processes, MFC is considered a next generation technology for wastewater industry, because it can be an energy positive system with net energy output, and it significantly reduces sludge production by more than 60\%\textsuperscript{3,17}. Over the past decade the MFC power output has been improved by several orders of magnitudes, but one main challenge for MFC to be used in large scale applications is the high cost compared to other wastewater treatment alternatives\textsuperscript{18}.

One of the major contributors to the high cost of MFCs is the electrode materials, which is estimated to amount to 20-50 \% of the overall cost\textsuperscript{19}. However, electrodes play a fundamental role in facilitating exoelectrogenic biofilm growth and electrochemical reactions and are essential in improving the functionality and efficiency of MFCs. Ideal electrode materials should possess key characteristics such as high surface area, high conductivity, low cost, and biocompatibility\textsuperscript{20}. Most electrode materials used in MFCs are carbon based granular activated carbon (GAC) or graphite granules (GGs)\textsuperscript{20}, especially in larger scale systems, because GAC has high degree of microporosity and catalytic activities, and GGs are less expensive with higher conductivity, even though the surface area density is lower. The costs of GAC or GG electrodes range from 500-2500 US$ per US tonne, which is significantly lower than carbon cloth or carbon paper
(100,000-500,000 US$ per tonne), but it is still considered high for large scale applications. In addition to the cost, the life-cycle impact of these materials can be significant depending on feedstock choice, manufacturing, and disposal methods. For example, GAC is most commonly manufactured from the pyrolysis of coal along with secondary thermal or chemical activation\textsuperscript{21,22}. GGs can be mined from natural deposits or synthetically manufactured through the thermal treatment (>3000°C) of carbon based materials. Such feedstock extraction and manufacturing methods used for industrial GAC and GG can be highly energy intensive and result in the release of environmental pollutions, including CO\textsubscript{2} and other greenhouse gases. Furthermore, the recycle and reuse rate of GAC and GG are low, and the waste materials are traditionally landfilled after several times of usage.

In order to promote sustainable and cost-effective electrode materials, the feedstock, manufacturing, and end-of-life alternatives all need to be investigated. In this context, biomass-derived black carbon (biochar) could be a more sustainable option, because it is produced from locally available biowastes, such as agricultural and forestry residue, which helps lower the cost and environmental impact while ensuring a steady regional supply. Manufacturing is carried out through pyrolysis or gasification, which utilizes the internal chemical energy of the feedstock to fuel the carbonization process and produce harvestable bioenergy. In addition, unlike GG or GAC, biochar can be reused as agricultural soil amendment, which has been shown to increase crop production\textsuperscript{23,24}, increase microbial diversity and abundance, lower emissions such as NO\textsubscript{2}, and remain environmentally stable for thousands of years. Moreover, the cost of biochar is low, ranging from 51-381 US$ per ton\textsuperscript{25}, nearly ten times less than GAC and
GGs. Based on different purposes of usage, tailored biochar can be manufactured to have different physical properties\textsuperscript{26-28}. For example, by using elevated temperatures (>800-1000°C), biochars can have a wide range of pore sizes and high service area, which can also cause internal graphitization and increased conductivity\textsuperscript{29-31}.

Although the unique features of biochar have been demonstrated for some time in other areas, to our best knowledge few study investigated the feasibility and performance of biochar as electrode material in MFCs. In this study, we tested the performance of two different types of biochar materials made from compressed lodgepole pine sawdust pellets (BCp) and lodgepole pine woodchips (BCc) and compared them to GAC and GG as the anode materials in two-chamber MFCs. Performance was comprehensively characterized through electrochemical and statistical analyses, in terms of power production, resistivity, and total surface area. Furthermore, we also investigated the manufacturing process, feedstock selection, and cost of biochar electrodes.

![Four electrode materials used in this study](image1.jpg)
Experimental Section

Anode Electrode Material Manufacturing

The main physical characteristics and costs of the four anode materials used in this study are shown in Table 1, and their images are shown in Fig. 1a. Fig. 1b illustrates the general outlines of the manufacturing process for the electrode materials. The GAC was purchased from Cameron-Yakima, Inc, (Yakima, WA, USA), and it was manufactured from coal using industrial standard methods$^{21}$, resulting in 100% of activated carbon. Activation was achieved using thermal activation procedures. GG were purchased from Graphite Sales, Inc, (Nova, OH, USA). GG material is comprised of 100% synthetic graphite made from petroleum coke using temperatures exceeding 3000°C. BCc and BCp were both manufactured using a custom made top-lit up-draft biomass gasifier with an external fan, as described by Kerns et.al. 2012$^{32}$. Biomass was carbonized using a HHT of 1000°C, residence time of 1 hr, and a ramp rate of 16°C/min (figure X) and temperature reading were measured using a programmable thermocouple. BCp used compressed lodgepole pine sawdust pellets and BCc used lodgepole pine woodchips gathered from local forestry residue as the biomass feedstock.

Table I Electrode characteristics used in this study

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Particle size (mm$^3$)</th>
<th>Surface Resistance (Ω mm$^{-1}$)</th>
<th>Average Pore Diameter (Å)</th>
<th>BET SA (cm$^2$ g$^{-1}$)</th>
<th>Cost ($ Ton^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>26-36</td>
<td>8±2</td>
<td>26.8</td>
<td>1247.8</td>
<td>500-2500</td>
</tr>
<tr>
<td>GG</td>
<td>350-450</td>
<td>0.4±0.5</td>
<td>71.0</td>
<td>0.44</td>
<td>500-800</td>
</tr>
<tr>
<td>BCp</td>
<td>60-74</td>
<td>6±1</td>
<td>37.6</td>
<td>428.6</td>
<td>100-199</td>
</tr>
<tr>
<td>BCc</td>
<td>160-700</td>
<td>3±1</td>
<td>29.4</td>
<td>470.0</td>
<td>51-384</td>
</tr>
</tbody>
</table>
**MFC Construction and Operation**

MFCs were constructed using two polycarbonate cube-shaped blocks separated by a cation exchange membrane (38 cm², CMI-7000, Membrane International, NJ, USA). A 37 cm diameter hole was drilled at the center of each block forming the internal anode and cathode. Plain carbon cloth (38 cm², Fuel Cell Earth) was used as the common cathode material for all reactors. Each anode material (GAC, GG, BCp or BCc) was packed into one side of anode chamber to a volume of 75mL and held by a plastic mesh to tighten anode packing. A twisted titanium wire was used as a current collector and was buried in the packed anode. The total empty volumes were 150ml and 200ml for cathode chamber and anode chamber, respectively. MFCs were inoculated using anaerobic sludge from Longmont Wastewater Treatment Plant (Longmont, CO, USA). The anolyte growth medium contained 1.25 g of CH₃COONa, 0.31 g of NH₄Cl, 0.13 g of KCl, 3.32 g of NaH₂PO₄·2H₂O, 10.32 g of Na₂HPO₄·12H₂O, 12.5 mL of mineral solution, and 5 mL of vitamin solution per liter. The catholyte was potassium ferricyanide solution dissolved in 50 mM phosphate buffer, which aims to provide a stable cathode potential and minimize cathode limitation on system comparison. Each MFC was operated in fed-batch mode under a 400 ohm external resistor. When voltage dropped below 20 mV, both anolyte and catholyte were replaced with fresh media. All the tests were conducted at room temperature and repeated for at least 3 times.

**Statistical and Electrochemical Analyses**

The surface resistance measurement was determined by randomly selecting 35 electrode samples and measuring the ohmic resistance across a 4 mm distance with a programmable multimeter. The t-distribution was used to calculate confidence intervals.
(CIs). The 95% CIs were calculated by $X \pm 2.032S/\sqrt{n}$, where $X = \sum_{i=1}^{n} X_i/n$ was sample mean, $S = \sqrt{\left(\sum_{i=1}^{n}(X_i - X)^2\right)/(n - 1)}$ was sample standard variation, and $n$ was the sample size$^{33}$.

The cell voltage (E, volt) and electrode potentials for each MFC were measured continuously using a data acquisition system (Keithley Instrument, OH) every 66 sec. Polarization curves were obtained by varying external resistances from 50,000 to 30 ohm with each resistor stabilized for 30 min$^{13}$. The anode potential and cathode potential were measured against an Ag/AgCl reference electrode (RE-5B, Bioanalysis) inserted in the anode chamber and cathode chamber, respectively. During both acclimation and fed-batch periods, circuits were operated under a fixed load (Re, ohm) of 400 Ω. Current (I, amp) was calculated according to $I = E/Re$. Power (P, watt) was calculated according to $P = EI$. Current density and power density were normalized by cathode projected surface area of 38 cm$^2$. Electrochemical impedance spectroscopy (EIS) was conducted by a potentiostat (PC 4/3000, Gamry Instruments, NJ, USA) to determine total internal resistance using the anode as the working electrode, where the cathode served as the counter electrode and reference electrode$^{14,34}$.

Brunauer–Emmett–Teller (BET) method that uses a five-point N$_2$ gas adsorption technique (ASAP 2020; Micromeritics, Norcross, GA) was used to measure specific surface area and pore size distribution of the electrode materials. Average pore size and pore size distribution were determined from desorption of N$_2$ according to the method developed by Barrett, Joyner, and Halenda (BJH)$^{33,36}$. 
Results and Discussion

Power Production from Electrode Materials

The maximum power output and Columbic efficiency (CE) are two major measures to evaluate the performance of MFC systems. The CEs and maximum power densities from MFCs occupied with the 4 different anode materials (BCp, BCc, GAC, and GG) are summarized in Table 2 and Fig. 2, and the power densities are normalized by cathode surface area. Results showed that the GAC anode achieved the highest CE at around 47%, and GG had the lowest CE at 35%. The CEs from BCc and BCp were comparable at 41-43%. GAC had the highest power density of 674 ± 10 mW/m$^2$, followed by GG with 566 ± 5 mW/m$^2$, BCp with 532 ± 18 mW/m$^2$, and BCc with 457 ± 20 mW/m$^2$ (Table 2). The power output from BCp and BCc was 21% and 32% lower than the GAC, and 6% and 19% lower than the GG anodes. Fig. 2B shows that the cathode potentials among all 4 reactors were comparable as designed, because ferricyanide cathode was used to minimize the cathode effects. The anode potential of BCc increased to around 0 mV at 1.8 A/m$^2$, which resulted in lower power output. It was hypothesized that the difference in power densities can be attributed to the difference in both surface area density and system internal resistance, which will be explained in more detail in the following sections. It must be noted that the power density differences are not an intrinsic value of the biochar material, and it could be manipulated through variations in manufacturing. As research in this field matures, biochar electrodes could be manufactured in such a way to mimic the beneficial properties of both GAC and GG, while maintaining its integrity as a sustainable electrode material option. More detailed synopses of the manufacturing alternatives will also be discussed in the following
sections. Moreover, when material costs were added into consideration, Table 2 shows that to generate the same amount of 1 W electricity, the biochar based electrodes (BCp and BCc) were much more cost effective than GAC and GG, in fact more than ten times cheaper, indicating a good potential in larger scale applications.

![Power density curve normalized by cathode projected area (A) and electrode potentials (cathode, filled symbols; anode, open symbols) versus Ag/AgCl reference electrode as a function of current density in two-chamber reactors packed with GAC, GG, BCp and BCc.](image)

**Figure VIII.** Power density curve normalized by cathode projected area (A) and electrode potentials (cathode, filled symbols; anode, open symbols) versus Ag/AgCl reference electrode as a function of current density in two-chamber reactors packed with GAC, GG, BCp and BCc.

**Surface Characteristics of Electrode Materials**

High surface area and low resistance are two fundamental characteristics to define good electrode materials and affect MFC power output performance. While this section discusses the characteristics of surface area and porosity of the four materials, the next
section elucidates the effects of resistance. Table 1 and Figure IX show the pore distribution of the materials using the Brunauer–Emmett–Teller (BET) test. Results show that GAC has the highest BET surface area of 1247.8 cm²/g followed by BCp and BCc with 469.9 cm²/g and 428.6 cm²/g respectively. GG had the lowest BET surface area of 0.44 cm²/g. The pore size distribution for GAC is concentrated around 20-30 Å, while the BCp and BCc samples had an average pore diameter of 30-40 Å range.

![Incremental pore area with the distribution of pore size](image)

**Figure IX Incremental pore area with the distribution of pore size**

While the high surface area can explain why GAC obtained a higher power density, as it presumably has high microbial attachment and therefore more electron transfer, it is hard to directly correlate the low surface area of graphite with low power output. As shown in the Figure VIII, graphite electrode generated higher power density than the biochar electrode despite its low surface area, and it is believed mainly due to the high conductivity of graphite.
Studies show that surface area and pore size can be due to a variety of factors including the manufacturing process and feedstock material. The higher surface area of GAC is primarily caused by the secondary activation process carried out during manufacturing, in which reactive components of the feedstock material were burn away by the use of oxidizing agents, such as steam or carbon dioxide, leaving behind a pitted and porous char\textsuperscript{21,37}. The biochar samples used in this study and GGs did not undergo this activation step, but the gasification process used to manufacture both biochar samples is thought to promote the formation of higher BET surface area similar as GAC. The gasification process reached a highest treatment temperature (HTT) of 1000\(^{\circ}\)C with a heating rate of 16.6\(^{\circ}\)C/min (figure 5), and in the process lignocellulosic materials are converted to a primarily aromatic carbon-based char\textsuperscript{38}. The HTT and heating rate are reported to significantly influence the physical structure of the feedstock material during carbonization. For example, studies showed that higher surface area was achieved at temperatures between 650\(^{\circ}\)C and 850\(^{\circ}\)C,\textsuperscript{39,40,41} but sintering and deformation may occur at higher temperatures\textsuperscript{41}. Brown, et. al. provides further evidence that higher surface area is achieved with higher heating rate and is primarily due to cracking at low temperatures by unevenly heating the feedstock material. These cracks provided access to internal pores that could not be as easily effected by melting and deformity of the feedstock material at high temperatures. Brown, et. al.\textsuperscript{42} provides further evidence that higher surface area is achieved with higher heating rate, because such process leads to cracking at low temperatures by unevenly heating the feedstock material, and these cracks provided access to more internal pores.
Along with HTT and heating rate, the inherent porosity and structure of the feedstock material can also affect the surface area density. Several studies showed that biomass based chars possess high surface area so can be cheaper surrogates for GAC type electrode materials. In many cases, the archetypal cellular structure of the parent feedstock material is identifiable in chars derived from botanical origin, resulting in a honeycomb-like structure that significantly contributes to the majority of macroporosity. Although there is a growing body of literature on the effects of manufacturing methods on the chemical and physical properties of biochar and other biomass based absorbance materials, there is little understanding of how surface area density and pore size distribution effects microbial growth, abundance, and adhesion. This study highlights that microporosity is important for increased power density, but additional research is needed to refine the manufacturing of biochar in order to increase the desired

**Figure X Temperature profile and residence time of BCp and BCc gasification**

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characteristics as MFC electrodes while maintaining the economic and environmental benefits.

**Resistance Characteristics of Electrode Materials**

Similar as surface area, internal resistance ($R_i$) is one of the major factors affecting power density in MFCs. The total $R_i$ can be separated into activation resistance ($R_p$), ohmic resistance ($R_o$) and concentration resistance. $R_p$ occurs when electrons are transferred to or from a compound, primarily during oxidation/reduction reactions and relates to the catalytic efficiency near or on the electrode surface. The concentration resistance is due to the rate of mass transport to or from the electrode. While $R_o$ occurs due to the resistance of electron and ion transfer through the solution, electrodes, and membrane. Electrochemical impedance spectroscopy (EIS) is a technique used to measure chemical and physical processes in solution and can help to separate out the different internal resistances in MFC reactors. By graphing the data collected from EIS and constructing a Nyquist plot, $R_i$, and $R_s$ can be calculated (Figure XI). According to our EIS results, GG has the lowest $R_s$ of $24 \pm 0.6 \, \Omega$, followed by BCc with $29 \pm 0.7 \, \Omega$, BCp with $34 \pm 0.3 \, \Omega$, and GAC with $34 \pm 0.9 \, \Omega$ (Table 2). The surface resistance results can be seen in Table 1 with GG having $0.4 \pm 0.5 \, \Omega \, \text{mm}^{-1}$, followed by BCc with $3 \pm 1 \, \Omega \, \text{mm}^{-1}$, BCp with $6 \pm 1 \, \Omega \, \text{mm}^{-1}$, and GAC with the highest surface resistivity of $8 \pm 2 \, \Omega \, \text{mm}^{-1}$. However, GG and GAC had a similar total $R_i$ of $39 \pm 9 \, \Omega$ and $40 \pm 3 \, \Omega$ respectively, while BCp and BCc had a higher $R_i$ of $46 \pm 2 \, \Omega$ and $43 \pm 3 \, \Omega$ respectively (Table II).

The $R_s$ is responsible for nearly $86\%$, $62\%$, $74\%$, and $68\%$ of the total $R_i$ in the GAC, GG, BCp, and BCc, reactors respectively, but cannot account entirely for the
difference in the observed power densities. The $R_p$ for BCp and BCc was 7 ± 0.9 Ω and 8 ± 0.1 Ω respectively, much higher than GAC with 4 ± 0.6 Ω and GG with 4 ± 0.2 Ω. Because of the biochars lower $R_s$ compared to GAC, it is believed that the $R_p$ is the primary reason for the differences in power density. It is generally accepted that the catalytic activity of the anode is due primary to microbial biomass density and surface area density and combined have been shown to positively correlate with $R_p$. GAC’s lower $R_p$ and lower $R_i$ can thus be explained by its higher surface area density, which makes up for its higher $R_s$. When comparing BCp with BCc, the differences in power density can also be attributed to differences in surface area density. Although BCp has higher BET surface area and a lower surface resistance, its larger particle size limits its surface area density, which results in a higher $R_p$ and resulting higher $R_i$.

![Figure XI System resistance of the reactors filled with four different anode materials](Figure XI System resistance of the reactors filled with four different anode materials)
Our results further emphasize the need to develop electrodes with high surface area density and low resistance. However, this should not come at higher costs or environment impact. The development of graphitic structures in biomass-based electrode material is due to the thermal treatment of the carbonaceous feedstock material, where carbon rearranges into small graphitic crystallites at temperature 700°C-800°C\textsuperscript{30,31}. These graphitic zones have delocalized pi electrons that facilitate the flow of electrical current. Resistance through the graphitic zones is based on the degree of purity and orientation. Other studies have shown that biomass treated at high temperatures can have both high surface area and low resistance and could function as electrodes or supercapasitors\textsuperscript{43,44}. Converting non-conductive biomass into electrode materials has been demonstrated and because of the stored chemical energy in the feedstock material could be energy positive, but further research is needs to develop the optimal methodology to achieve maximum surface area and conductivity while reducing the amount of energy and environmental impact. Doing so could help to lower the cost of electrode material, increase the feasibility of scaling up MFC technologies, and reduce environmental impact.

**Biochar Electrode Life-Cycle and Cost Analysis**

There are a variety of feedstock materials and manufacturing technologies used to make biochar, but it is generally accepted that high-yield, low emission pyrolysis and gasification biochar manufacturing and land application is as a way to simultaneously sequester carbon, produce energy and increase crop production. The methods employed to make biochar with high surface area density and low resistance could be emphasized to produce electrodes materials for MFCs while maintain its environmental and economic
benefits. Moreover, the use of biochar as an electrode material in MFC reactors, especially for wastewater treatment, could add an additional step to further expand its life-cycle benefits and in doing so could also reduce the cost and increasing the feasibility of large-scale deployment of MFCs.

Biochar’s carbon (C) sequestration potential is largely due to conversion of biomass C to biochar C, a much more recalcitrant form which slows the rate at which photosynthetically fixed C returns to the atmosphere\(^{45}\). This conversion process sequesters around 50% of the biomass C, significantly greater than that retained from burning (3%) or biological decomposition (<10-20% after 5-10 years)\(^{46}\). Using higher temperatures (>800°C), such as those employed to make high surface area and conductive chars increases fixed C ratio and stability of the material\(^{47}\). Although the yields from high temperature treatments are often lower, much of the loss in weight is due to the off gassing of volatile organic components of the feedstock. GAC and GG also have high concentrations of C, but when coal is used as the feedstock material, the C is derived from fossil sources and is not part of the current cycle. The pyrolysis of coal only increases the total atmospheric C concentration, along with other toxic substances such as mercury and sulfur. This further emphasizes the importance of feedstock material and manufacturing methods when determine the impact of electrode materials.

Similar to GAC, any carbonaceous material could be used as a feedstock in the production of biochar electrodes. Biowastes, such as forestry, milling, and agricultural residue, along with yard clippings and construction waste are the feedstock of choice because of their reliable supply, low cost, high lignin content, and high surface area and conductivity when manufactured at high temperatures\(^{48}\). Coal is most commonly used in
GAC manufacturing because of its lower cost and high carbon content. However, using biowaste with little to no commercial value and local availability greatly reduces the cost of feedstock purchasing compared to coal. In this study we used lodgepole pine chips and lodgepole pine sawdust pellets as the feedstock material. Both of these materials are locally available and are either considered biowaste or made from biowaste. Data on U.S. supplies suggest that 0.012 Pg C yr\(^{-1}\) and 0.024 Pg C yr\(^{-1}\) of biochar could be produced from forestry residue and mill residue\(^{46}\). This is a stark comparison when you consider that there are no graphite mines in the U.S. and few globally\(^{49}\). Although feedstock characteristics and availability are important to ensure a high quality product and to maintain a steady supply, manufacturing methodology also contributes significantly to the environmental impact, final characteristics and cost of manufacturing biochar electrodes.

### Table II List of MFC reactors in this study and their specifications

<table>
<thead>
<tr>
<th>Anode Material</th>
<th>Total BET SA (m(^2))</th>
<th>(R_s (\Omega))</th>
<th>(R_i (\Omega))</th>
<th>Maximum Power Density (mW/m(^2))</th>
<th>Maximum Power Density (W/m(^3))</th>
<th>CE (%)</th>
<th>Material Cost (US$)/W(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>3.68</td>
<td>34.9</td>
<td>40.3</td>
<td>674±10</td>
<td>7.32±10</td>
<td>47±0.7</td>
<td>$402.80</td>
</tr>
<tr>
<td>GG</td>
<td>0.002</td>
<td>24.9</td>
<td>39.9</td>
<td>566±5</td>
<td>6.15±5</td>
<td>35±0.1</td>
<td>$392.62</td>
</tr>
<tr>
<td>BCp</td>
<td>0.52</td>
<td>34.3</td>
<td>46.2</td>
<td>532±18</td>
<td>5.78±18</td>
<td>41±0.4</td>
<td>$23.88</td>
</tr>
<tr>
<td>BCc</td>
<td>0.32</td>
<td>29.7</td>
<td>43.4</td>
<td>457±20</td>
<td>4.97±20</td>
<td>43±0.1</td>
<td>$35.79</td>
</tr>
</tbody>
</table>

\(^a\) Material cost per Watt produced was calculated by dividing electrode material cost in anode chamber by maximum power density

As described above, biochar is the result of the pyrolysis or gasification of biomass. The elevated temperatures needed to carbonize the feedstock material are generally produced by the combustion of the syngas released during pyrolysis of the feedstock. In this way, the chemical energy stored in the feedstock material is used to...
fuel the carbonization process. The manufacturing of GAC also uses a similar technique but often times an additional energy source is used to control the reaction rate and fuel thermal activation. Biochar does not traditionally undergo activation, but air flow through the reactor during gasification can perform similar purposes. The biochar samples used in this experiment were manufacturing using a top-lit up-draft gasifier (TLUD). In a TLUD the “pyrolysis front” moves downward through the mass of fuel, converting the biomass to char. The syngas is directly combusted at the top of the kiln, increasing the internal temperature and passively pulling air up through the bottom. The air flowing through the reactor is thought to react with the surface of the char material, similar to the activation step in GAC, increasing the surface area density. This is achieved with minimal external energy. TLUD gasifier is just one example of variety technologies that can be used to manufacture biochar electrodes, pyrolysis, gasification, hydrothermal, and flash carbonization being the most thoroughly study\textsuperscript{25}. No matter what technology is employed, high yield, low emissions, and parameters that increase the surface area and conductivity should be emphasized to produce the most sustainable and cost effective electrode materials possible.

Figure XII Flow chart of manufacturing methods of electrode materials used in this study
Along with energy production, land application of biochar has shown additional C offsets and cost reductions. The benefits of biochar addition to agricultural soils includes improved water and nutrient retention, increase crop yield, suppressed N$_2$O emissions, reduce fertilizer requirements, and increased soil organic carbon content$^{50}$. We suggest that composting and soil application of spent MFC electrode material, especially in the case of wastewater treatment, could also have similar, if not increased, beneficial effects on agricultural production. Several studies have shown that high surface area biochars have increased absorbance capabilities$^{51,52}$. When used as an electrode material in MFCs treating wastewater, valuable micronutrients could be adsorbed and slowly released in agricultural field after application. The thick exoelectrogenic biofilm established on the biochar electrode surface during wastewater treatment could also help to increase the biological diversity and abundance in agricultural soils. If sorbed contaminates or pathogens are of concern, composting could be utilized to allow ample time for elevated temperatures and enhanced microorganism activity to biodegrade any pollutants. However, recent research on biochar and carbon absorbents has shown little migration of pathogens or leaching form contaminated materials$^{53}$. If sufficient evidence is collected to demonstrate the beneficial use of spent biochar electrodes as agricultural amendments, it could significantly offset the cost of MFC construction and operation.

It is evident that additional research is needed to refine the production method and full life-cycle use of biochar electrode materials. Great care should be taken to select feedstock material with little economic value, while maximizing the energy output during manufacturing. Manufacturing parameters should also be set to produce chars with increased surface area density and conductivity to increase their performance in MFCs.
Additional research is also needed to test the feasibility of land application of spent biochar electrodes.

**Conclusion**

High temperature biochar materials, made from lodgepole pine chips (BCc) and lodgepole pine sawdust pellets (BCp), were tested for the first time as an electrode materials in a microbial fuel cell. BCp and BCc should satisfactorily power density of 532 ± 18 mW m⁻² and 457 ± 20 mW/m⁻² respectively compared to 674 ± 10 mW m⁻² and 566 ± 5 mW m⁻² for GAC and GG respectively. Differences in power density can be attributed to the lower surface area density than GAC and high surface resistance than GG. However, biochar electrode material cost have been estimated at 51-356 US$/tonne, up to ten times cheaper than GAC (500-2500 US$/tonne) and GGs (500-800 US$/tonne). Biochar electrode manufacturing also carries additionally environmental benefits, including biowaste feedstock, energy positive manufacturing, and carbon sequestration potential. We also suggest spent biochar electrode material could be used as an agricultural amendment, further increasing its life-cycle benefits and subsidizing its cost. Although further research is needed to optimize the manufacturing method of biochar electrode production and increase its performance, the use of biomass-derived electrode materials ring in a new era of material use in MFCs with additional economic and environmental benefits.
CHAPTER IV

BIOCHAR LCA AND CARBON ACCOUNTING

Introduction

Global atmospheric greenhouse gas (GHG) concentrations are rapidly increasing and concerns about anthropogenic climate change are sparking interest in carbon sequestering technologies. Although there are several methodologies being explored, biochar production and its use as a soil amendment has been gaining worldwide attention due to its carbon sequestering potential, benefits to the agricultural sector, co-energy generation, and its use of waste-biomass as a feedstock material.

Biochar is a crude form of activated carbon produced through the combustion of biomass, in a limit oxygen environment, with the attentional use as an agricultural amendment. Pyrolysis and gasification are the most widely used and thoroughly studied methods of manufacturing, where high temperatures and controlled oxygen exposure are used to convert biomass into primarily recalcitrant carbon. Biochar is comprised mostly of carbon (97%), ash (3%) and some trace minerals (<1%), although the physical and chemical features vary greatly depending on feedstock and manufacturing methods. The volitization of organic matter from the original feedstock material creates syngas that can be further combusted, for co-energy generation, or refined to produce bio-oils.

Traditionally biochar has been used as an agricultural amendment, in most cases, increasing crop yield and decreasing the need for fertilizers. Depending on soil type, biochar can help mitigate N2O emissions from agricultural soil. It is also used in land reclamation projects, because of its water and nutrient absorption capabilities. And
more recently, biochar is being investigated as a low cost electrode material in microbial fuel cells.

Biochar has the potential to sequester carbon because of its biomass feedstock use, high carbon content, and stability during use\textsuperscript{45}. However, there have been few case studies investigating that “real-world” production of biochar. More research needs to be done in order to quantify the total GHG emissions during the production of biochar compared to the amount of carbon being sequestered in its final use and that of the traditional fate of the biomass. There have been several LCA conducted on biochar\textsuperscript{45,50,56}, but they have only focused on hypothetical examples and theoretical models. In this study we take direct emissions data from field based slow-pyrolysis biochar production using forestry residue, and compare it to the more common treatment methods, field burning and decomposition.

**Goal and Scope**

The goal of this study is to calculate the total carbon balance and GHG emissions of biochar production compared to the more traditional fate of forestry residue. Using 1 kg of biomass as the functional unit, a process-based LCA analysis is used to inventory total GHG emissions (CO\textsubscript{2}, N\textsubscript{2}O, and CH\textsubscript{4}) released during biochar production and transportation. The carbon content of the biochar and the GHGs associated with the alternative fate scenarios is also subtracted from the GHG inventory of production and the carbon sequestration potential is assessed.
Research Methodology

An LCA analysis is conducted according to commonly excepted procedure. The entire life cycle of biochar production is evaluated from cradle to grave. The transportation data was collected and compiled from EPA emission reports\textsuperscript{57}. The emissions and technical process specifications was collected from reports and consultations given by the facility managers themselves. Emissions associated with the alternative fate of forestry residue were taken from a Stockholm Environmental Institute report\textsuperscript{58}.

Case Study: Biochar Production in Golden Colorado

Company Description

Biochar Engineering Corporation (BEC) is a design fabrication company in Golden Colorado that focuses on biochar and co-energy production. BEC optimizes its biochar production for high sorption properties and fixed carbon content. Their pyrolysis machines are designed for mobility and can be transported on-site of biomass storage locations, reducing the need to transport the biomass feedstock.

Technology Description

BEC uses a two-stage process with their Beta Base Unit (a mobile \(\frac{1}{4}\) ton/hr production unit). During the first stage the material is carbonized in an aerobic environment. Temperatures at this stage range between 700-750\(^\circ\)C, for a duration of less than one minute. By controlling the ratio of air to biomass, they can ensure that it is kept below the combustion ratio. Using this process they can also ensure the preservation of solid carbon. During the second stage the material is kept in a sweep gas environment at
temperatures between 200-500°C for approximately ten to fifteen minutes. The gas produced by the pyrolysis of biomass in the first stage, which is mostly composed of N₂, H₂, CO, CH₄ and higher VOCs and trace gases, is used as the sweep gas in second stage. Biochar ranging from 1.5 cm long by 1 cm wide and .5 cm thick is produced.

**System Boundary**

The system boundary includes the on-site collection and processing of forestry residue to chip, the processing of chip to biochar, and the transportation of biochar to end-use customers. This process is consistent with the real world production of biochar using BEC technology. We did not include the GHG mitigation associated with the end-use of biochar in our LCA because there is no consistent scientific data and depends on several variables including soil type, application rate, and local climate. For comparison, we used GHG emissions data on more tradition forestry residue fates. In most cases the residue left behind after a forestry operation is collected, piled, and burned (11). In some cases the residue is scattered and left to decompose. For the purpose of this analysis we compare the GHG emissions from the on-site decomposition and combustion of forestry residue.

**Figure XIII. Flow Diagram for Biochar production**
Data Collection Methodology

Forestry Residue Processing

Forestry residue is mostly comprised of small diameter trees, branches, and the tops of commercial timber collected during logging operations. We assumed that the material has dried and all of the needles have fallen off. This method is consistent with other forestry residue analyses\textsuperscript{58,60,61}. Collection and processing operation was modeled after the current operations of Grays Harbor Paper and Hermann Bros. GHG emissions associated with the collection and processing of the forestry residue was collected from the Stockholm Environmental Institute report, “Greenhouse gas and air pollution emissions of alternatives for woody biomass residues”.

Pyrolysis Emissions

Stack emissions were collected from BEC, using methods that are required by the EPA for air pollution reporting. The biomass feedstock used during the emissions testing was comprised of chipped forestry residue, mostly lodgepole pine chip. Some propane and electricity use for the pyrolysis process is also calculated into the total emissions.

Transportation Emissions

The emissions associated with the transportation of biochar to the end-user was collected from the EPA vehicle emissions report\textsuperscript{57}. Biochar was assumed to be transported with a semi for 200 miles round trip with a 10 mpg average. 100 miles is the average distance from forestry operations in the Rocky Mountains to agricultural field on the front range of Colorado.
**On-site Decomposition and Combustion of Forestry Residue**

Emissions data associated with the on-site decomposition and combustion of forestry residue was collected from the Stockholm report. Emission factors and data resources relied on current published literature, reports, site visits, and air emissions data reported by state agencies. For on-site decomposition it is assumed that the material is scattered and left to decompose, emissions are associated with a decay period of over 100-yr. Although, some reports indicate methane emissions associated with decomposition, this report assumes that residue piles do not facilitate anaerobic conditions and there is no methane release. For the on-site combustion it is assumed forestry residue is gathered into piles and ignited by hand.

**Biochar Stable Carbon Content**

Data on the stable carbon content was collected from laboratory elemental analysis carried about by BEC.
GHG Inventory and Carbon Accounting

**Figure XIV. Carbon accounting of biochar production with avoided carbon loss due to combustion of forestry residue**

<table>
<thead>
<tr>
<th>Activity</th>
<th>t CO2e/ t-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gath/Chipping</td>
<td>0.008</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>0.297</td>
</tr>
<tr>
<td>Transportation</td>
<td>0.076</td>
</tr>
<tr>
<td>Biochar</td>
<td>-0.125</td>
</tr>
<tr>
<td>Avoided CO2e (Combustion)</td>
<td>-0.475</td>
</tr>
<tr>
<td>Total C</td>
<td>-0.218</td>
</tr>
</tbody>
</table>

**Figure XV. Carbon accounting during the production of biochar with avoided carbon loss due to decomposition of forestry residue**

<table>
<thead>
<tr>
<th>Activity</th>
<th>t CO2e/ t-1</th>
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</thead>
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<td>0.076</td>
</tr>
<tr>
<td>Biochar</td>
<td>-0.125</td>
</tr>
<tr>
<td>Avoided CO2e (Decomposition)</td>
<td>-0.395</td>
</tr>
<tr>
<td>Total C</td>
<td>-0.138</td>
</tr>
</tbody>
</table>
Results and Discussion

Global Warming-GHG Emissions

The total avoided CO$_2$e is -333 t CO$_2$e/t$^{-1}$ and -0.083 t CO$_2$e/t$^{-1}$ for the combustion and decomposition avoidance scenarios respectively. According to our results, the total GHG emissions associated with the production and transportation of biochar is negative, if you consider the avoided CO$_2$e due to combustion or decomposition of the feedstock. Of the total GHG emissions during the processing of biochar, pyrolysis is responsible for the majority or 79% of the total GHGs emitted. Much of the reduction in GHG emissions can be contributed to the use of a waste feedstock that would otherwise be combusted or decompose on-site. The mobile unit also allows the production of biomass on-site without the additional need to transport the feedstock before processing.

Carbon Accounting

The total C sequestered during the processing of biochar is -.189 t C/t$^{-1}$ and -.109 t C/t$^{-1}$ for the combustion and decomposition avoidance scenarios respectively. This indicates that there is more C sequestered during the processing of biochar than there is if the fate of the forestry residue was on-site combustion or decomposition. Much of the carbon sequestration can be attributed to the avoidance of on-site combustion or decomposition; however the stable C content of the biochar contributes 20% of the total carbon sequestration.

Process Refinement Recommendations

Although our results indicate that the production of biochar using forestry residue is GHG and carbon negative there is room for further improvement, including co-
production of heat and power. Co-production of heat and electricity would off-set the use of fossil fuel combustion and/or natural gas. Many pyrolysis machines incorporate co-production into their systems. Utilizing the syngas and heat produced during the pyrolysis process, electricity and heat can be used for domestic consumption. In the Denver region, 1.75 lb or CO2e is emitted per kWh, depending on the pyrolysis machine design; this would offset the amount of GHG released into the atmosphere if a traditional method of electricity production is used.

**Conclusion**

The production of biochar using waste biomass material has great potential to sequester C and mitigate GHG emissions. There have been several LCAs published claiming this potential, however they use hypothetical models and do not have real-world data. To our knowledge there has not been an LCA conducted on actual case studies of the production of biochar. This report is the first to get direct emissions data on real-world production and use of biochar. The findings of this report demonstrate that biochar production can sequester C and mitigate GHG emissions if waste forestry residue is used as feedstock instead of its alternative fates. Although the findings show GHG mitigation, there is still room for improvement, including co-production of electricity and heat, which would further improve the technology.
CHAPTER V

CONCLUSION

The goal of this thesis was to demonstrate the possibility of microbial fuel cells (MFCs) for treating wastewater and to use biochar as a more sustainable electrode material option in MFCs. These studies demonstrate that in fact MFC technology can treat wastewater as effectively as traditional aeration treatment, although further research is needed to improve the process. The studies also show that biochar could effectively serve as a surrogate for more traditional electrode materials with lower overall cost and environmental impact. These results could be highly impactful with the potential to change the current global wastewater treatment infrastructure from one that is costly, energy intensive, or in the case of developing countries, lacking all together.
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