

# Thermodynamic Analysis of a single chamber Microbial Fuel Cell

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# 1 Introduction

Renewable energy (RE) applications are becoming a popular means of power generation within our society. Microbial fuel cells (MFCs) are new form of renewable energy technology that can generate electricity from what would otherwise be considered waste. According to the Logan Group of Pennsylvania State University (PSU), this technology can use bacterium already present in wastewater as catalysts to generating electricity while simultaneously treating wastewater (Lui et al., 2004; Min and Logan, 2004). Although MFCs generate a lower amount of energy and efficiency than that of Proton Exchange Membrane (PEM) fuel cells, a combination of both electricity production and wastewater treatment would reduce the cost of treating primary effluent wastewater. Most of the research performed on MFCs is concerned with increasing the power density of the system with respect to the peripheral anode surface area. Currently, these studies report values of chemical oxygen demand (COD) removal efficiencies and Coulombic efficiencies. To the author's knowledge, there are no research publications available to the public containing second law thermodynamic efficiencies of a MFC. A first law efficiency of a MFC is not a desired value to obtain due to the complex composition of domestic wastewater.

During the 2005 Fall semester, the author received a \$100 research grant from the Friends of the Arcata Marsh (FOAM) in support of developing a better knowledge base and skills associated with MFC technology. With this award, and donations from the Schatz Energy Research Center (SERC), E-TEK and Ballard Power Systems; the author obtained materials to build 7 different single chamber MFCs. The single chamber MFCs were modeled after one developed at Pennsylvania State University (PSU). The author tested these MFCs with primary effluent domestic wastewater. The author obtained a Nature Area Use permit granted by the City of Arcata to sample domestic wastewater from the Arcata Wastewater Treatment Facility. The direct current voltage potential data obtained from these MFCs was then used to compute second law thermodynamic efficiencies of a MFC based on thermodynamic principles and experimental data.

# 2 Problem Formulation

The objective of this study is to describe the basic characteristics of the MFC system, analyze key strategies for improving or maximizing the performance of the MFC system, and discuss the environmental significance of the MFC system. Analysis will include: determining the

theoretical electromotive force of a MFC by analyzing the oxidation of acetate by bacteria at the anode and the reduction of oxygen at the cathode, relating the theoretical electromotive force of the MFC to that of the measured voltage potential of a MFC by calculating second law thermodynamic efficiencies, and identifying potential losses including an overall analysis of the quantifiable environmental significance of an MFC.

### 3 Literature Review

The purpose of this literature review is to organize relevant information to use as a reference when applying principles of research and experimentation to MFC technology. This section contains an overview of the biological mechanism, design structure of a single chamber MFC, and thermodynamic properties associated with a MFC.

#### 3.1 Biological Mechanism

The basics of microbial catabolism consist of an oxidation/reduction process between a substrate and an enzyme (Bennetto 1990). This normal oxidation/reduction process consists of an electron transfer that can be harnessed in a MFC due to the characteristics of certain bacteria or microbes (Bond et al. 2002). The bacteria identified in MFCs are known as *Shewanella putrefaciens*, *Geobacter sulfurreducens*, *Geobacter metallireducens* and *Rhodospirillum rubrum* and are commonly identified anywhere from marine sediments to domestic wastewater (Bond et al. 2003; Bond et al. 2002; Lui et al. 2004). Some research suggest that these bacteria will directly transfer an electron to any type of conductive material (Bond et al. 2003, Min 2004). In the case of a MFC, this conductive material is known as the anodic electrode and the cathodic electrode.

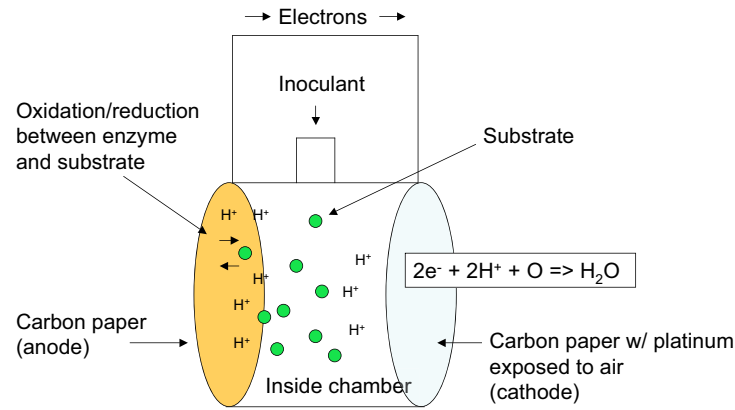


Figure 1: Representation of Anaerobic (anode portion) and Aerobic (cathode portion) Biological Degradation Simultaneous to Electricity Generation in a single chamber Microbial Fuel Cell (Zielke 2006)

A simple representation of the biological mechanism is shown within a single chamber MFC (Figure 1). The anode portion consists of an oxidation/reduction process which produces a hydrogen gradient and allows hydrogen protons to diffuse to the cathode portion to balance out the pH of the organic matter or wastewater originally introduced to the biological organisms in a MFC. The cathode portion also consists of this oxidation/reduction process; however, since the cathode allows oxygen to diffuse from the air to the inside portion of the single chamber MFC, water can be formed without a formation of a hydrogen proton gradient. The energy available from the proton gradient due to the anode can be harnessed by connecting a circuit from the anode to the cathode to allow the electron, oxygen and the hydrogen protons to catalytically form water via a platinum catalyst (Bond and Lovely 2003, Bond et al. 2002, Lui et al. 2004). Note that the mechanism of MFC technology is still in research stages and many possible reasons for electricity generation cannot be answered without a better understanding of the characteristics of the electricity generating bacteria in MFCs (Min 2004).

### 3.2 Design Structure

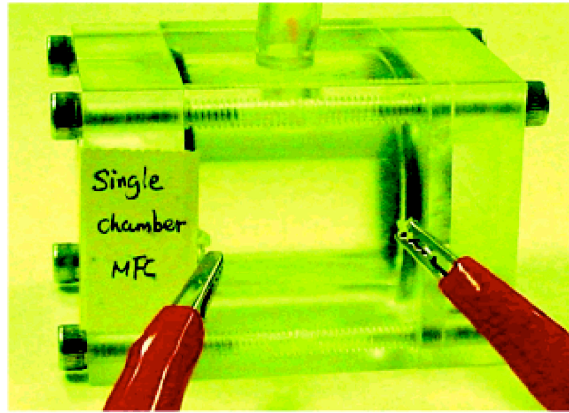


Figure 2: Representation of a single chamber Microbial Fuel Cell designed at Penn. State University (Lui and Logan 2004)

Typical MFCs consists of two separate chambers which can be inoculated with any type of carbon source liquid (i.e. biological oxygen demand (BOD) contributing liquid). These two chambers consist of an anode chamber and a cathode chamber and are generally separated by a PEM (Oh and Logan 2004). PEM fuel cell researchers know that PEMs are designed to allow oxygen from the air to react at the cathode (Lui and Logan 2004). The Logan Group suggest that this same principle can be used to design a single chamber MFC. A single chamber MFC is where the anode chamber is separated from the cathode chamber by a gas diffusion layer (GDL) or gas diffusion membrane (GDM) allowing for a passive oxygen diffusion to the cathode (Figure 2).

### 3.3 Thermodynamic Principles

Similar to that of a galvanic cell, the change in energy and entropy, the heat energy dispersed or absorbed and the useful energy produced or consumed in a MFC system is subject to the laws of thermodynamics (Rossini 1950). For this reason, limiting a thermodynamic analysis to known reversible chemical reactions that take place within the MFC simplifies calculations. However, this limits the thermodynamic analysis to that of the second law efficiency calculations instead of including first law efficiency calculations. Given a known reversible chemical reaction, a calculation of the Gibbs free energy can be expressed as (Bard



1985, Newman 1973),

$$\Delta G_r = \Delta G_r^0 + RT \ln(\Pi)$$

where

$$\begin{aligned} \Delta G_r &= \text{Gibbs free energy} \\ \Delta G_r^0 &= \text{Gibbs free energy under standard conditions} \\ R &= \text{universal gas constant} \\ T &= \text{absolute temperature} \\ \Pi &= \text{reaction quotient of the products divided by the reactants} \end{aligned}$$

According to researchers of the Logan Group, the Gibbs free energy under standard conditions is calculated from the tabulated energies associated with the formation for organic compounds in aqueous solutions (Logan 2006). The negative value of the Gibbs free energy is known as the maximum work of the system and can be deduced to terms of the overall cell electromotive force (emf) as follows (Logan 2006),

$$-\Delta G_r = W_{max} = E_{emf} \cdot (Q) = E_{emf} \cdot (n \cdot F)$$

where

$$\begin{aligned} W_{max} &= \text{maximum theoretical work} \\ E_{emf} &= \text{potential difference between the cathode and anode} \\ Q &= \text{charge} \\ n &= \text{number of electrons per reaction} \\ F &= \text{Faraday's constant} \end{aligned}$$

Rearranging the above equation yields,

$$E_{emf} = -\frac{\Delta G_r}{(n \cdot F)}$$

And under standard conditions,

$$E_{emf}^0 = -\frac{\Delta G_r^0}{(n \cdot F)}$$

Using the afore mentioned equations, an expression for the overall electromotive force of a particular reaction at any condition can then be calculated as,

$$E_{emf} = E_{emf}^0 - \frac{RT}{nF} \ln(\Pi)$$

The Logan Group indicates that this generic equation for the electromotive force could be used for each half-reaction that takes place at the cathode and at the anode. The amount of research needed to evaluate every half-reaction that takes place would be beyond the scope of this project. In general, the electromotive force of the MFC, under specific conditions, can then be calculated as (Logan 2006),

$$E_{emf} = E_{cathode} - E_{anode}$$

where

$$\begin{aligned} E_{cathode} &= \text{electromotive force of a specific reaction taking place at the cathode} \\ E_{anode} &= \text{electromotive force of a specific reaction taking place at the anode} \end{aligned}$$

The MFC second law efficiency can be evaluated by relating the theoretical electromotive force to the measured cell potential based on the assumption that the simple reactions evaluated at the anode and cathode are similar to that of the more complicated reactions involved with the bio-degradation of wastewater,

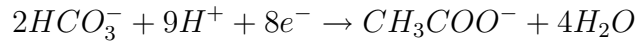
$$\eta_{MFC} = \frac{W_{actual}}{W_{max}} = \frac{V_{measured} \cdot (n \cdot F)}{E_{emf} \cdot (n \cdot F)} = \frac{V_{measured}}{E_{emf}}$$

where

$$\begin{aligned} \eta_{MFC} &= \text{MFC second law efficiency} \\ W_{actual} &= \text{actual work output} \\ V_{measured} &= \text{measure voltage potential} \end{aligned}$$

## 4 Methodology

One common anode half reaction that is analyzed by both the Logan Group and researchers around the world is that of the amino acid acetate since acetate is a common constituent of domestic wastewater (Microbial Fuel Cell 2006). This half reaction that takes place at the anode can be expressed as (Logan 2006),



A calculation of the electromotive force at the anode for the biological oxidation of acetate is as follows (Logan 2006),

$$E_{anode} = E_{anode}^0 - \frac{RT}{8F} \ln \left( \frac{[CH_3COO^-]}{[HCO_3^-]^2[H^+]^9} \right)$$

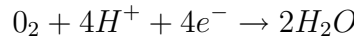
where

$$\begin{aligned} E_{anode}^0 &= 0.187V (\text{Logan 2006, Thauer 1977}) \\ R &= 8.31447 \frac{J}{mol \cdot K} \\ T &= 298K \\ H^+ &= 1M \end{aligned}$$

and using an assumption by that of the Logan Group for the concentration of products and reactants (Logan 2006),

$$\begin{aligned} HCO_3^- &= 5mM \\ CH_3COO^- &= 5mM \\ pH &= 7 \end{aligned}$$

a calculation produces a potential of -0.296 V. This same type of methodology can be used for the simple reaction of oxygen reduction at the cathode (Logan 2006),



where a calculation of the electromotive force at the cathode is as follows (Logan 2006),

$$E_{cathode} = E_{cathode}^0 - \frac{RT}{4F} \ln \left( \frac{1}{pO_2[H^+]^4} \right)$$

where

$$\begin{aligned} E_{cathode}^0 &= 1.229V (\text{Logan 2006, Thauer 1977}) \\ R &= 8.31447 \frac{J}{mol \cdot K} \\ T &= 298K \\ H^+ &= 1M \end{aligned}$$

and using an assumption by that of the Logan Group for the concentration of products and reactants (Logan 2006),

$$\begin{aligned} pO_2 &= 0.2 \\ pH &= 7 \end{aligned}$$

a calculation produces a potential of 0.805 V. Overall, the maximum amount of voltage potential in a MFC with acetate oxidation and oxygen reduction is the cell emf of,

$$E_{emf} = 0.805 \text{ V} - (-0.296 \text{ V}) = 1.101 \text{ V}$$

Typical measured potential values of MFCs range somewhere around 0.2 V (Logan 2006). A value of 0.2 V is much lower than even the lowest value of only oxidation reduction at 0.805 V. Calculation of first law efficiencies for each experimental MFC developed at Humboldt State University by the author will use 1.101 V as the maximum voltage potential based on the assumption that the simple reactions evaluated at the anode and cathode are similar to that of the more complicated reactions involved with the bio-degradation of wastewater.

The direct current (DC) voltage data obtained from the single chamber MFCs exhibited a double layer effect at the electrodes. In general, the double layer effect will affect DC voltage readings over time. This attribute requires further investigation beyond the scope of what is required by this class. Dr. William Golden of the Humboldt State University - Dept. of Chemistry suggested developing an experiment to relate alternating current (AC) to DC; however, after this experiment was conducted, it cannot be shown that there is a linear relationship between AC and DC. A Microsoft Excel Anova Table was used to analyze this relationship (Appendix B). The next suggestion was to use only the first values obtained for DC voltage assuming that the double layer effect has not taken place during the first voltage readings (Appendix A).

## 5 Results and Discussion

This section exhibits the data of second law efficiencies, a system analysis of potential voltage losses, and an overall emission reduction.

### 5.1 Thermodynamic Efficiency

A representation of the second law thermodynamic efficiencies are tabulated for each individual MFC developed at Humboldt State University using a maximum voltage of 1.101V and experimental values of direct current voltage (Table 1).

Table 1: First Law Thermodynamic Efficiencies from Experimental Data

	Thermodynamic Efficiency
MFC 1	7.27%
MFC 2	18.2%
MFC 3	20.0%
MFC 4	7.27%
MFC 5	7.27%
MFC 6	33.6%
MFC 7	9.99%

The large differences of efficiency values between the MFCs can be accounted for by an insufficient biofilm presence on the anode and cathode portions of the MFC and operating temperature differences. A low efficiency value indicates that the MFC is not working correctly.

## 5.2 System Analysis

According to the Logan Group, potential losses include: (1) bacterial metabolism losses, and (2) activation losses (Logan 2006). The bacterial metabolism losses are caused by differing pH values and redox ratios of products to reactants, since these are generally difficult to accurately determine (Logan 2006). An in depth analysis of fluctuating pH values and the redox ratios associated with domestic wastewater bio-degradation would be useful in pin-pointing areas of voltage potential losses. In regard to activation losses, many researchers suggest lowering the activation energy to minimize potential losses (Logan 2006). Lowering this activation energy can be accomplished by increasing the anode and cathode surface area, increasing the amount of electrode catalyst (typically platinum), increasing the temperature, and establishing a sufficient amount of biofilm on each electrode (Logan 2006).

## 5.3 Overall Emission Reduction

Without taking any embedded energy into account for the fabrication of a MFC, a MFC is a zero emission device. The Arcata Wastewater Treatment Facility receives 2 million

gallons of domestic wastewater per day which requires two primary clarifiers, each sized to 45 *ft* diameter and 7.5 *ft* tall or 11,928 *ft*<sup>3</sup> (or 338 *m*<sup>3</sup>) area. Note that a simple trickling filter exhibits 100  $\frac{m^2}{m^3}$  and an average of 240  $\frac{mW}{m^2}$  is obtained from a typical MFC (Logan 2005). Assuming half of the volume of the primary clarifier tank as volume for the platinum catalyzed cathode material, an approximation of power generation can be calculated as follows,

$$\frac{338 \text{ } m^3}{2 \times 100 \frac{m^2}{m^3}} (240 \frac{mW}{m^2}) = 4.053 \text{ } kW$$

Note that a typical power demand at a wastewater facility is only 1,500 *W* at any given time. Due to the large expense of platinum catalyzed cathode material, a cost-effective approach would include sizing the MFC to meet the demand of a typical wastewater facility (which uses 1.5 *kW*  $\times$  8,750 *hrs* in one year = 13,140 *kWh* in one year). Assuming that this wastewater facility is located in Arcata, CA with electrical connections to the PG&E electrical grid which emits 0.064  $\frac{kg \text{ } C}{kWh}$ , a total carbon emission offset can be computed as follows (Marney et al. 2002),

$$Total \text{ } C = 13,140 \text{ } kWh \times 0.064 \frac{kg \text{ } C}{kWh} = 841 \text{ } kg \text{ } C \text{ per year}$$

Note that the emissions from the PG&E electrical grid will fluctuate over time, so an emission offset over any long length of time would be difficult to accurately determine (e.g. 30 years).

## 6 Conclusion

The results of this project indicate that electricity generation can be obtained by use of a single chamber MFC to analyze the thermodynamic attributes and the quantifiable environmental significance of an MFC. Specifically, the investigation shows the following:

- Second law thermodynamic efficiencies of a single chamber MFC will range from 7.27% to 33.6% depending on system performance or lack of.
- An overall theoretical carbon emission offset by the Arcata Wastewater Treatment Facility utilizing MFC technology is 841 *kg C per year*

## 7 Further Investigation

The results of second law thermodynamic efficiencies could not be compared to that of other studies since these types of studies do not yet exist to the best of the author's knowledge. Further research is needed to understand the reasons for the obtained results.

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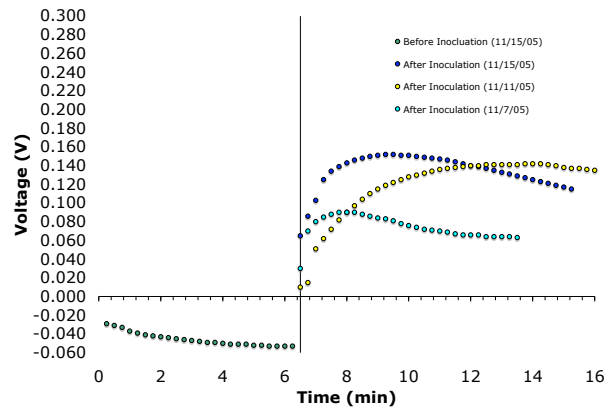
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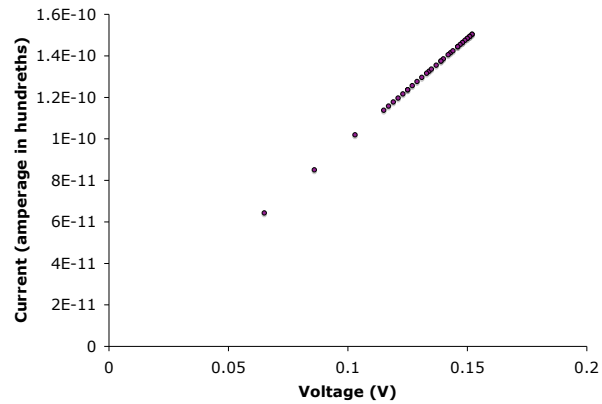


## 9 Appendix

### 9.1 Appendix A



(a)



(b)

Figure 3: Logged data of MFC number 1; (a) voltage readings over time in minutes (b) corresponding I-V curve

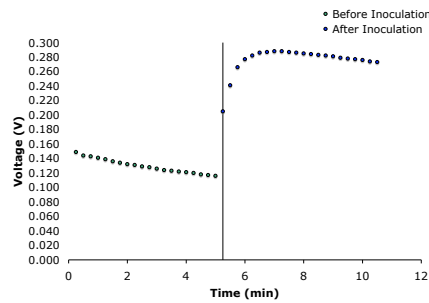


Figure 4: MFC number 2 voltage readings over time in minutes

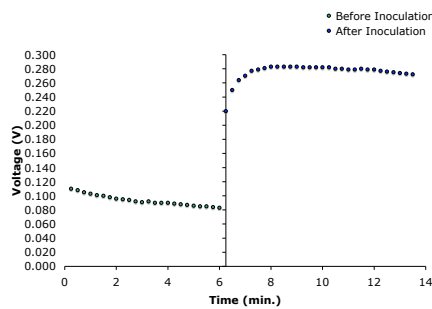


Figure 5: MFC number 3 voltage readings over time in minutes

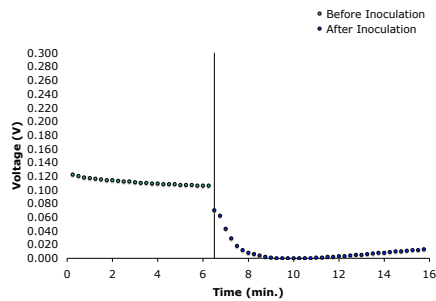


Figure 6: MFC number 4 voltage readings over time in minutes

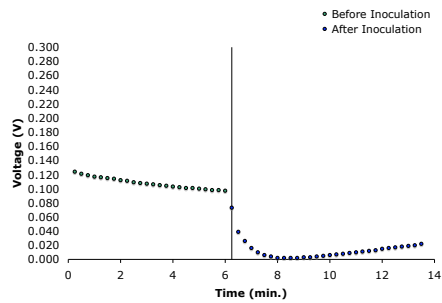


Figure 7: MFC number 5 voltage readings over time in minutes

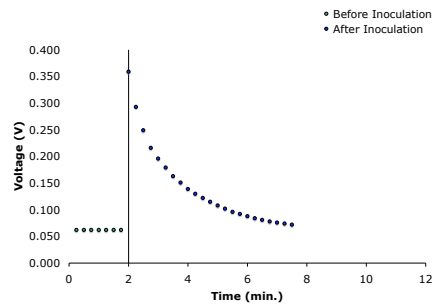


Figure 8: MFC number 6 voltage readings over time in minutes

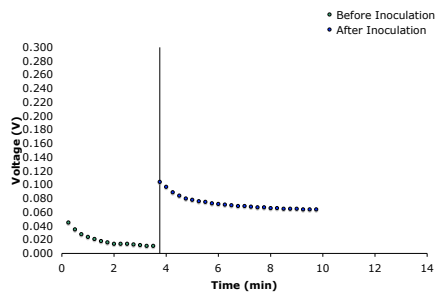


Figure 9: MFC number 7 voltage readings over time in minutes

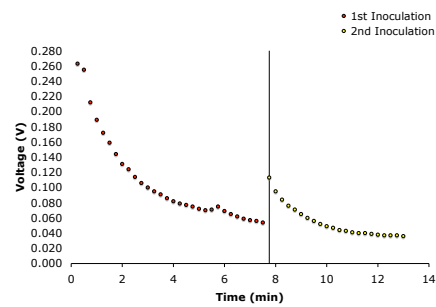


Figure 10: MFC control 1 voltage readings over time in minutes

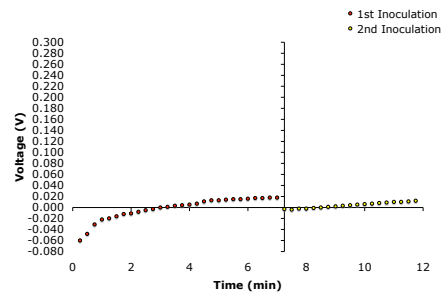


Figure 11: MFC control 2 voltage readings over time in minutes

## 9.2 Appendix B

### SUMMARY OUTPUT

Regression Statistics					
Multiple R	0.08979145				
R Square	0.0080625				
Adjusted R Sq	-0.19032499				
Standard Error	0.00867605				
Observations	7				

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	3.0591E-06	3.0591E-06	0.04064019	0.84817906
Residual	5	0.00037637	7.5274E-05		
Total	6	0.00037943			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%
Intercept	0.00384076	0.01104628	0.34769739	0.7422261	-0.02455461
X Variable 1	-0.06528662	0.32385184	-0.20159411	0.84817906	-0.89777429

There isn't a significant linear relationship between ac and dc (p-value from model utility)  
 The slope isn't significantly different from zero (p-value=0.59)

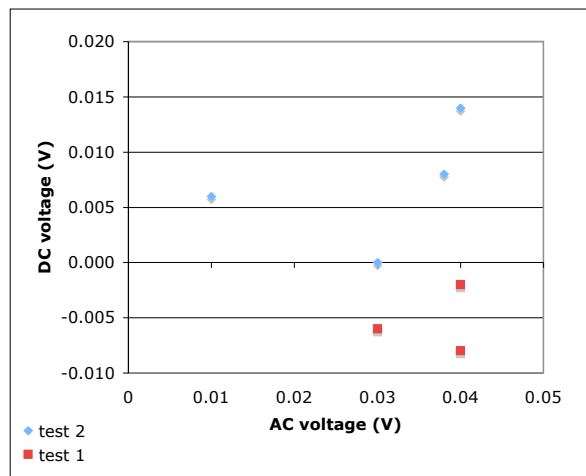


Figure 12: Rejection of the Hypothesis that a Linear Relationship Exists between AC and DC Voltage Potential