Numerical Investigation of Double Chamber Acetate-Fed Microbial Fuel Cell in Unsteady-State Condition

I Subadri¹, A Satriyatama¹, I D M Budi¹, A Harimawan¹*

¹Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Bandung, Bandung 40134, Indonesia
*Email: intan_subadri@students.itb.ac.id

Abstract. Microbial fuel cells (MFCs) are devices that utilize the work of microorganisms to oxidize organic substrate involving biochemical pathways. Several studies have been done based on experiments while simulation and modelling remain unexplored. Basically, MFCs have a lot of similarities to chemical fuel cell systems, which modelling and simulation have been widely developed. Hence, a study should be done to develop the model in order to widen the implementation of MFCs. In order to evaluate MFCs performance with less cost and time, numerical modelling might be an effective approach. Models could be easily developed or modified for various operation conditions and configurations to generate experimental data on MFCs. A number of papers on simulation and modelling focused on cell voltage as function of both cell current density and chemicals concentration. In this paper, a double chamber acetate MFCs under continuous operation and unsteady state condition would be investigated. MFCs model based are developed by calculating biochemical reactions, Butler-Volmer equation, and electrochemical equations using MATLAB 2018a software. The parameters and constants data reported from recent literature are used. Results show that periodic flow rate of fuel could improve the power production. This result also gives the prediction of cell voltage and current density. Nevertheless, models with various conditions or configurations could be developed to scale-up or create more efficient MFCs using simple methods.

1. Introduction
The energy crisis in recent year, including electricity has become a global issue in this world. It is happened because of the massive use of fossil fuels, that is equal to 50.66%, reported by Dudley in 2018. In fact, fossil fuels are not a sustainable energy source since fossil fuel cannot be renewed and is decreasing year by year. Moreover, the use of fossil fuels actually contributes to the land degradation, CO₂ emission in the atmosphere, and also water pollution. These phenomena have led to the development of sustainable and eco-friendly energy.

Microbial fuel cell (MFC) is a electrochemical cell that could convert chemical energy into electrical energy via biochemical reactions directly. MFC utilizes energy from organic substrates by using exoelectrogenic microorganisms [1]. Regarding MFC applications, the ability of microorganisms to utilize organic materials, can be found in wastewater, biosensors, and chemostat assays [2]. Moreover, MFC can also be used in desalination, hydrogen production, pollution remediation, and remote power source [3]. MFC could be operated in the ambient temperature, neutral pH, and atmospheric pressure. Power production from organic substrate is one of most interest areas in MFC. The MFC technology may become great promise since effective and wide scale MFC are not available yet.
Multiple chemical, biological, and physical indicators have an important role to determine MFC work performance [4]. The analysis of a MFC system requires many discipline knowledges to achieve better understanding. Efforts have been made to analyze the aspects related to microorganisms such as molecular analysis, biochemical rate, and internal electron transfer [4, 5]. Problems faced by MFC such as stability, reliability, and electricity production efficiency must be fixed before putting into larger scale operation.

Researches have been developed to investigate the molecular reaction of the electron transfer and microbial community while recent studies have been focusing on engineering and electricity calculation. The variations of the organic compound’s concentration, biological environment, load disturbance, and the number of microbes is directly affected by the current and voltage produced by the MFC. Therefore, it is important to analyse the complexity of the MFC to provide complete understanding of the high-bioelectrochemical performance to maintain the price, reproducibility, and process control of the MFC.

Pinto et al. [6] proposed the two populations model to describe the competition of anodophilic and methanogenic microbes. Later, models by Zeng et al. [5] were developed, explained the MFC model as function of biochemical, Butler-Volmer, and mass balances expression. Picoreanu et al. [1] developed the model predictive control for MFC performance improvement. Capodaglio et al. [7] published the mathematical model related to MFC application in wastewater treatment. Then, Oliveira et al. [8] reported an MFC model, focused on parameters such as substrate concentration, current density, and cell temperature.

In this paper, the MFC studies are generally divided into three main sections, which are biochemical reaction process, thermodynamic studies, and electrochemical process. With the development of mathematical modelling, the non-linear and hysteresis characteristic of the MFC can be solved using MATLAB. As a result, the optimum condition of the MFC to provide constant current and voltage output is obtained.

2. Methods
In this research, simulation platform is established mainly based on Zeng et al. [5] MFC model. Zeng and teams developed a model close to chemical-based fuel cells. Biochemical reactions, mass/charge balances, and Butler-Volmer expression are integrated on two-chamber configuration to simulates unsteady behavior of MFC. Modelling methods described are applied for making some modification [9, 10].

Considering acetate as substrate on anode compartment, the mass balance equation is considered in the equation (1) [11]. Since the anode compartment is operated under anaerobic conditions, the acetate reaction could be modelled with Monod-type equation. In electrochemical cell, the bioelectrochemical reactions are controlled by the electrical potential. Butler-Volmer expression (2) can be used to mathematise the reaction rate [12].

\[
(\text{CH}_2\text{O}_2) + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8\text{H}^+ + 8e^- \quad (1)
\]

\[
r_1 = k_1^0 \exp \left( \frac{aF}{RT} \eta \right) \frac{c_{\text{ac}}}{K_{\text{ac}} + c_{\text{ac}}} X \quad (2)
\]

In cathode compartment, the reduction of dissolved oxygen described in Eq. (3). The Monod-type behavior of dissolved oxygen shows that oxygen reduction is ignorable [13]. The rate of reaction formula in cathode compartment explained in Eq. 4.

\[
\text{O}_2 + 4e^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^- \quad (3)
\]

\[
r_2 = -k_2^0 \frac{c_{\text{O}_2}}{K_{\text{O}_2} + c_{\text{O}_2}} \exp \left[ (\beta - 1) \frac{F}{RT} \eta_c \right] \quad (4)
\]
The continuously stirred tank reactor (CSTR) is assumed in anode and cathode compartment. Hence, mass transport, phase mixture, and redox reactions is assumed to be fast processes. In addition, acetate and carbon dioxide are assumed not diffuse to membrane, transportation loss is neglected, and fluid density in anode and cathode compartment is equal. The chemical components mass balances in anode compartment, which are acetate, dissolved CO₂, biomass, and H⁺ are described in following Eq. (5), (6), (7), and (8). The subscript ‘a’ denotes anode and ‘c’ denotes cathode.

\[ V_a \frac{dC_{Ac}}{dt} = Q_a (C_{Ac}^{in} - C_{Ac}) + A_m r_1 \]  
\[ V_a \frac{dC_{CO_2}}{dt} = Q_a (C_{CO_2}^{in} - C_{CO_2}) + 2A_m r_1 \]  
\[ V_a \frac{dC_H}{dt} = Q_a (C_{H}^{in} - C_H) + 8A_m r_1 \]  
\[ V_a \frac{dx}{dt} = Q_a \left( \frac{x^{in} - x}{f_x} \right) + A_m V_{ac} r_1 - V_a K_{dec} X \]  

Meanwhile, in the cathode compartments, the mass balances of dissolved O₂, OH, and M⁺ are written in following Eq. (9), (10), (11).

\[ V_c \frac{dC_{O_2}}{dt} = Q_c (C_{O_2}^{in} - C_{O_2}) + A_m r_2 \]  
\[ V_c \frac{dC_{OH}}{dt} = Q_c (C_{OH}^{in} - C_{OH}) - 4A_m r_2 \]  
\[ V_c \frac{dC_M}{dt} = Q_c (C_{M}^{in} - C_M) + N_m A_m \]  

The cell current density and the flux of ions relation can be described in Eq. 12.

\[ i_{cell} = F \sum_{i} z_i N_i \]  

\( N_i \) is the superficial flux, \( i_{cell} \) denotes the cell current density, and \( z_i \) is the charge number. It gives the charge balances at the anode and cathode as described below.

\[ C_a \frac{dy_a}{dt} = 3600i_{cell} - 8Fr_1 \]  
\[ C_c \frac{dy_c}{dt} = 3600i_{cell} - 8Fr_2 \]

It has been assumed that we neglect the electric connections and the ohmic drops in the current-collectors. The total potential or the cell voltage \( U_{cell} \) is calculated using following equation.

\[ U_{cell} = U^0 - \gamma a + \gamma c - \left( \frac{d_m}{k_m} + \frac{d_{cell}}{k_{aq}} \right) i_{cell} \]

\( d_{cell} \) and \( d_m \) are distance of the electrode and membrane thickness. \( k \) represents the conductivities characteristic. To determine the overpotential of the MFC, the approximation of Butler-Volmer equation, Tafel equation is used. Tafel equation can be written as below.

\[ i = nFKC \exp(\pm \alpha F \left( \frac{et \eta}{RT} \right)) \]

The microorganism biofilm formation in this model is observed. The chemotaxis equations below us used to determine the production rate of the sensing molecules from attached and suspended bacteria

\[ \frac{\partial E}{\partial t} = D_E \frac{\partial^2 E}{\partial Z^2} - \lambda E + \alpha_s x_s \]
E is the sensing molecule concentration and $D_E$ is the coefficient of it. $\lambda$ is the sensing molecule degradation rate, while $\alpha_s$ is the sensing molecule production rate. The boundary conditions are defined as following.

$$D_E \frac{\partial E}{\partial Z}(z = 0) = \alpha X$$

(18)

$$\frac{\partial E}{\partial Z}(z = l) = 0$$

(19)

The first boundary condition is defined for the biofilm formed on the surface of the anode. The second boundary condition is defined for the membrane. The chemotaxis equation of suspended microorganism is described below.

$$\frac{\partial x_s}{\partial t} = \mu S E_0 \frac{\partial^2 x_s}{\partial x^2} - X \frac{\partial}{\partial Z} \left( x_s \frac{\partial x_s}{\partial Z} \right) + \gamma x_s q_s$$

(20)

The boundary condition for the condition is described as below.

$$\frac{\partial x_s}{\partial Z}(Z = 1) = 0$$

(21)

The bacteria is sticking on the anode surface so that the bacteria density is assumed to be zero.

$$x_s(Z = 0) = 0$$

(22)

The main of the microbial fuel cells are modeled and simulated using MATLAB 2018a software of two-chamber. The model also can be used to simulate the running of MFC in various conditions. All parameters, constant, and assumptions are given in Table 1.

| Symbol | Description | Unit | Value |
|--------|-------------|------|-------|
| $F$ | Faraday’s constant | Coulombs mol$^{-1}$ | 96485.4 |
| $T$ | Temperature | K | 303 |
| $R$ | Gas constant | J mol$^{-1}$ K$^{-1}$ | 8.314 |
| $A_m$ | Area of membrane | $m^2$ | $5 \times 10^{-4}$ |
| $Y_{ac}$ | Bacterial yield | Dimensionless | 0.05 |
| $K_{dec}$ | Decay constant for acetate | h$^{-1}$ | $8.33 \times 10^{-4}$ |
| $f_x$ | Reciprocal of wash-out fraction | Dimensionless | 10 |
| $V_a$ | Volume of anode compartment | $m^3$ | $5.5 \times 10^{-5}$ |
| $V_c$ | Volume of cathode compartment | $m^3$ | $5.5 \times 10^{-5}$ |
| $Q_a$ | Flow rate of fuel feed to anode | $m^3$ h$^{-1}$ | $2.25 \times 10^{-5}$ |
| $Q_c$ | Flow rate feeding to cathode compartment | $m^3$ h$^{-1}$ | $1.11 \times 10^{-3}$ |
| $C_{in}^{Ac}$ | Concentration of influent acetate in anode compartment | mol $m^{-3}$ | 1.56 |
| $C_{in}^{CO_2}$ | Concentration of influent CO$_2$ in anode compartment | mol $m^{-3}$ | 0 |
| $X_{in}$ | Concentration of influent bacteria in anode compartment | mol $m^{-3}$ | 0 |
| $C_{in}^{H}$ | Concentration of influent H$^+$ in anode compartment | mol $m^{-3}$ | 0 |
| $C_{in}^{O_2}$ | Concentration of dissolved O$_2$ in the influent of cathode compartment | mol $m^{-3}$ | 0.3125 |
| $C_{in}^{M}$ | Concentration of influent M$^+$ in cathode compartment | mol $m^{-3}$ | 0 |
### Concentration of OH⁻ in cathode compartment

\[ C_{OH}^{in} \]

\[ k_1^0 \] Rate constant of anode reaction at standard condition \( \text{mol m}^{-2} \text{h}^{-1} \)

\[ k_2^0 \] Rate constant of cathode reaction at standard condition \( \text{m}^{12} \text{mol}^{-4} \text{h}^{-1} \)

\[ K_{ac} \] Rate constant for acetate \( \text{mol m}^{-3} \)

\[ \alpha \] Charge transfer constant of anode Dimensionless

\[ \beta \] Charge transfer constant of cathode Dimensionless

\[ U^0 \] Cell open circuit potential volt

\[ x_s \] Suspended microorganisms concentration in liquid bulk \( \text{kg}_{\text{CODX}} \text{m}^{-3} \)

\[ m_{SEO} \] Mobility coefficient \( \text{cm}^2 \text{day}^{-1} \)

\[ \gamma \] Chemotactic coefficients of sensing molecules \( \text{kg}_{\text{CODX}} \text{kg}_{\text{CODS}}^{-1} \)

\[ q_{s,max} \] Substrate consumption in the anolyte \( \text{kg}_{\text{CODS}} \text{kg}_{\text{CODX}}^{-1} \text{day}^{-1} \)

### Results and Discussion

The predicted results on substrate concentration change, electrochemical analysis, and work efficiency in double chamber acetate-fed microbial fuel cell are described below.

#### 3.1 Reactions and Kinetic Study

For MFCs mass balances, the changes of all substrates and chemicals are considered. Meanwhile, the internal diffusion between substrate and biofilm are neglected. All the primary components in MFCs are represented in mass and charge balances, especially chemical and biomass. The predicted results of reaction rates and mass balances calculations expressed on Fig. 1 below.
Figure 1. Simulation results of acetate MFC a) reaction rates; b) Concentrations of chemical substances.

The component concentration of substrate and reaction rates are evaluated using all parameters listed in Table 1. Figure 1a shows that the reaction rate of oxygen reduction in cathode chamber and acetate oxidation in anode chamber increase proportionally with cell current density. This results could be explained by Eq. (12) and (13) integration.

Figure 1b explains the concentration changes of acetate, CO₂, biomass, M⁺, and dissolved oxygen during operation. From the plot, it can be seen that the decrease of acetate followed by the increase of CO₂ and biomass. The reactions also represent that the higher current density, the higher acetate will be consumed and CO₂ will be produced in anode chamber. Similar results also happened in cathode chamber, where dissolved oxygen decreased influenced by higher current density. This results could be confirmed based from Picoreanu et al. [14], where the acetate consumption was limited by the both electron acceptor and donor.

3.2. Electrochemical Model

The rate of an electrochemical reaction to the overpotential can be calculated using the Tafel equation. The electrode’ concentrations are assumed to be practically equal to the bulk electrolyte’ concentrations, so that the current can be expressed as a function of potential only [15]. Each data point is gained by simulating the Tafel equation in MATLAB. From anode and cathode potential, the output voltage of MFCs could be determined. The polarisation effect can cause the voltage losses since it can lead to the overpotential.
Figure 2. Results of activated potential loss as the function of a) current density and b) temperature.

Based on the graph above, the activated potential rises due to the increase of the current density. The raised of anode potential also influenced from the increased pH caused by acidified process at anode. The growth of the bacteria, that consists of 4 main points, affects the total current density. As the number of the bacteria grow, both the rate of acetate oxidation and oxygen reduction are faster and the cell current density. The kinetic reaction is faster when the temperature is increased. Therefore, the reaction will be directly shift to the right, then the anode product increases the activated potential loss.

3.3. Bacteria Distribution
The distribution of bacteria in anolyte of MFC is shown in Fig. 3. The trend of spatial distribution of suspended bacteria indicating the adsorption of suspended bacteria to biofilm. The variation of suspended bacteria indicates the two characteristics of bacteria movement, including bacteria diffusion and the bacteria movement as function of concentration gradient.

Figure 3. Biofilm concentration distribution.

The concentration of attached bacteria is increased by increasing the distance from anode that attributed to accessibility of nutrient in surface of biofilm which the net growth rate of these bacteria would be higher.
4. Conclusion

The mathematical models for MFCs work prediction are evaluated in this paper. The representative models from previous literature are investigated and applied. Mass and charges balance with bio-electrochemical reactions integration is used as the basis method. These results explain the trends in the simulated data in unsteady-state condition and the parameter’s influence for power production. Activated potential rises due to the increase of the current density and temperature. Overall, these mathematical models could provide a convenient tool for process optimization and process control further.

References

[1] Picireanu C, van Loosdrecht M C, Curtis T P, Scott K 2010 Model based evaluation of the effect of pH and electrode geometry on microbial fuel cell performance Bioelectrochemistry 78 8-24
[2] Choi S, Chae J 2012 An array of microliter-sized microbial fuel cells generating 100 μW of power Sensors Actuators A Phys. 177 10–15
[3] Pandey P, Shinde V N, Deopurkar R L, Kale S P, Patil S A, Pant D 2016 Recent advances in the use of different substrates in microbial fuel cells toward wastewater treat-ment and simultaneous energy recovery Appl. Energy 168 706–723
[4] Picireanu C, Head I M, Katuri K P, van Loosdrecht M C, Scott K 2007 A computational model for biofilm-based microbial fuel cells Water Res. 41 2921–2940
[5] Zeng Y, Choo Y F, Kim B H, Wu P 2010 Modelling and simulation of two-chamber mi-crobial fuel cell J. Power Sources 195 79–89
[6] Pinto R P, Srinivasan B, Manuel M F, Tartakovsky B 2010 A two-population bio-electrochemical model of a microbial fuel cell Bioresour. Technol. 101 5256–5265
[7] Capodaglio A G, Hlavínek P, Raboni M 2016 Advances in wastewater nitrogen removal by biological processes: State of the art review. Ambient. e Agua—An Interdiscip. J. Appl. Sci. 11 250.
[8] Oliveira V B, Simões M, Melo L F, Pinto A M F R A 2013 1D mathematical model for a microbial fuel cell Energy 61 463–471
[9] Pinto R P, Tartakovsky B, Srinivasan B 2012 Optimizing energy productivity of microbial electrochemical cells’ J. Process Control 22 (6) 1079–1086
[10] Corrêa J M, Farret F A, Canha L N, Simoes M G 2004 An electrochemical-based fuel-cell model suitable for electrical engineering automation approach IEEE Transactions on industrial electronics 51 (5) 1103-12
[11] Rozendal R A, Hamelers H V, Rabaey K, Keller J, and Buisman C J 2008 Towards practical implementation of bioelectrochemical wastewater treatment Trends in biotechnology 26(8) 450-459
[12] Kato Marcus, Andrew, César I Torres, and Bruce E Rittmann 2007 Conduction-based modeling of the biofilm anode of a microbial fuel cell Biotechnology and bioengineering 98.6 1171-1182
[13] Logan B E, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, Aelterman P, Verstraete W and Rabaey K 2006 Microbial fuel cells: methodology and technology Environmental science & technology 40 (17) 5181-5192
[14] Picireanu C, Katuri K P, Head I M, Van Loosdrecht M C M, Scott K 2008 Mathematical model for microbial fuel cells with anodic biofilms and anaerobic digestion Water. Sci. Technol 57 965–971
[15] Kazemi S, Barazandegan M, Mohseni M 2016 Systematic study of separators in air-breathing flat-plate microbial fuel cells – part 2: numerical modeling Energies 9 (2) 79