AN ABSTRACT OF THE DISSERTATION OF

Yu Miao for the degree of Doctor of Philosophy in Chemical Engineering presented on May 23, 2016.

Title: CO₂ Reduction in Microscale-Based Corona Reactor: Experiments and Modeling

Abstract approved:

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Global warming is becoming an increasingly important environmental concern and CO₂ is considered as the major cause of global warming. Creating useful applications for CO₂ would generate alternatives to merely venting CO₂ to the atmosphere, and decreasing the carbon intensity of human activities. Among various methods of CO₂ utilization, conversion of CO₂ to value-added chemical products is the most attractive. In this study, microtechnology and application of corona discharge are combined and introduced into CO₂ reduction process.

Experiments were conducted before the design and manufacture of the microreactor to determine the configuration of the reactor, products of reaction and effect of active volume ratio: (1) it is proved that through-gas corona discharge are much simpler to implement than through-liquid, especially those with high solubility of CO₂; (2) the V-I curve for the corona discharge reactors is characterized by a transition from a high voltage low current (which we call spark discharge) to a low voltage high current state (the corona discharge state), with this transition used as a diagnostic of the reactor operation in the corona discharge mode even when direct observation of the discharge is not practical; (3) the products for the reduction of dry CO₂ are carbon monoxide (CO) and oxygen (O₂), while for the reduction of wet CO₂, methane (CH₄) is also
formed in addition to these two products; (4) a larger active volume ratio results in higher conversion of CO₂ to products.

Based on the experimental results listed above, two multi-discharge microscale-based corona reactors were designed and manufactured. We found that for a needle-to-plate gap of 110µm, at the voltage of 0.840kV and current of 0.62mA, a flow of CO₂ and H₂O mixture (flow rate of CO₂ = 50sccm, CO₂-to-H₂O molar ratio = 1:2) can result in 5.5–6% conversion of CO₂ (with 40–50% conversion within the active volume of the reactor) with energy efficiency of 85–95%. The influence of the three main factors, namely the power applied to the reactor (specific points of the V-I curve used), flow rate of CO₂, and CO₂-to-H₂O molar ratio, on the performance and energy efficiency of the reactor were investigated. It was found that (1) the glow regime (or corona regime) is the optimal operation regime for this process from both conversion and energy efficiency perspectives, with higher current in this regime resulting in higher CO₂ conversion; (2) lower flow rate of CO₂ can result in higher conversion with lower energy efficiency, and conversely, the highest energy efficiency is achieved at the highest flow rate; (3) the conversion of CO₂ increases as the CO₂-to-H₂O molar ratio decreases, but the highest energy efficiency is achieved when this ratio matches the ratio of stoichiometric numbers.

A numerical model of the process reflecting the geometry, momentum balance, material balance and kinetics inside the reactor was developed to help understand the chemical reaction process. The reaction scheme was modelled as being driven by the initial cleavage of a CO₂ or H₂O molecule caused by collision with energetic electrons to produce CO+O or OH+H, followed by cascaded spontaneous reactions that yield the products. The reaction kinetics were approached as following pseudo-Arrhenius laws with a pre-exponential term k₀ and an exponential term, but rather than modelling the exponential term as dependent on temperature, the term was modelled as depending on the applied electrical potential in the corona discharge (i.e., rather than dependent on $e^{\frac{E_e}{RT}}$, it was modelled as dependent on $e^{\frac{E_e}{VF}}$, where $\beta$ is an
effectiveness parameter, $V$ is the applied electrical potential to the discharge, and $F$ is Faraday's constant). A refined parameter $n$ that defines the fraction of CO intermediate that either further fragment or remain as CO in the product stream, termed the kinetic parameter in this work, was also employed.

Optimization of the numerical model was applied to extract kinetic parameters for the CO$_2$ reduction process in the multi-point corona discharge with good agreement between simulated results and experimental data. The values of the final refined parameters were: for the initial dissociation of CO$_2$, the final values of the refined parameters were $k_{0,1} = 3.543 \pm 0.071 \times 10^{10} \text{sec}^{-1}$ and the electrical potential effectiveness parameter was $\beta_1 = 2.181 \pm 0.044 \times 10^1$, and for the dissociation of H$_2$O, the parameters were $k_{0,1} = 1.266 \pm 0.025 \times 10^8 \text{sec}^{-1}$, $\beta_4 = 8.403 \pm 0.168$, and the kinetic parameter $n = 0.50 \pm 0.010$. 


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Yu Miao

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

________________________________________
Yu Miao, Author
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NOMENCLATURE

\(a\) length of the triangular Teflon covers, unit: mm

\(a_1\) side length of the base of the needles on the 100-pin plate before improvement, unit: mm

\(a_2\) side length of the base of the needles on the 100-pin plate after improvement, unit: mm

\(A\) the saturation ionization constant for the gas at a particular \(E/p\) (electric field/pressure), unit: \((\text{Torr} \cdot \text{mm})^{-1}\)

\(A_i\) peak area in the \(i\)th measurement, unit: mV·sec

\(A_{\text{max}}\) maximum peak area, unit: mV·sec

\(A_{\text{min}}\) minimum peak area, unit: mV·sec

\(A_{\text{neighbor}}\) neighbor of the questionable measurement of peak area, unit: mV·sec

\(A_{\text{questionable}}\) questionable measurement of peak area, unit: mV·sec

\(\bar{A}\) average of the peak area, unit: mV·sec

\(b\) width of the triangular Teflon covers, unit: mm

\(B\) constant related to the excitation and ionization energies, unit: \(\text{V} \cdot (\text{Torr} \cdot \text{mm})^{-1}\)

\(C_{i,\text{exp}}\) experimental measured concentration of component \(i\), unit: mol/m³

\(C_{i,\text{mod}}\) simulated concentration of component \(i\), unit: mol/m³

\(C_{P,\text{fluid}}\) heat capacity of mixture CO\(_2\) and liquid water, unit: kJ/(mol·°C)

\(C'_{P,\text{fluid}}\) heat capacity of mixture CO\(_2\) and water vapor, unit: kJ/(mol·°C)
\( C_{P,\text{tube}} \) heat capacity of stainless steel tube, unit: kJ/(kg·°C)

\( d \) gap distance between the electrodes, unit: mm

\( d_i \) inner diameter of the evaporator, unit: m

\( d_o \) outer diameter of the evaporator, unit: m

\( D \) diameter of the footprint of corona discharge, unit: mm

\( D_i^{\text{m}} \) mixture-averaged diffusion coefficient, unit: m²/sec

\( D_i^{\text{T}} \) thermal diffusion coefficient, unit: kg/(m·sec)

\( D_{ik} \) multicomponent Maxwell-Stefan diffusivities, unit: m²/sec

\( e \) charge of an electron, unit: C

\( E \) external electric field, unit: V/cm

\( E_A \) activation energy, unit: eV

\( \dot{E}_{\text{electrical}} \) electrical energy flow, unit: J/sec

\( \dot{E}_{\text{external}} \) external energy flow, unit: J/sec

\( \dot{E}_{\text{in}} \) energy flow at the inlet, unit: J/sec

\( \dot{E}_{\text{out}} \) energy flow at the outlet, unit: J/sec

\( \Delta \dot{E}_{\text{system}} \) change of energy in the system, unit: J/sec

\( F \) Faraday constant, \( F = 96485 \text{C/mol} \)

\( F_{\text{loss}} \) friction loss, unit: J/kg

\( FN \) false negative test results, unit: dimensionless

\( F_{\text{obj}} \) objective function, unit: (mol/m³)²
\( F_{\text{obj,new}} \) new objective function calculated through numerical optimization, unit: \((\text{mol/m}^3)^2\)

\( g\Delta h \) change of potential energy, unit: J/kg

\( h \) Planck’s constant, \( h = 6.626 \times 10^{-34} \ \text{J} \cdot \text{sec} \)

\( h_1 \) height of the cylinder part of the tungsten needle, unit:mm

\( h_2 \) height of the tip part of the tungsten needle, unit:mm

\( h_3 \) height of needles on 200-pin plate, unit: mm

\( h_4 \) height of needles on 100-pin plate before improvement, unit: mm

\( h_5 \) height of needles on 100-pin plate after improvement, unit: mm

\( H \) height of reaction channel, unit: mm

\( H_1 \) height of the reaction channel after improvement, unit: mm

\( \overline{h}_f^0 \) enthalpy of formation for each species, unit: kJ/mol

\( \Delta \overline{h} \) change of specific enthalpy for each species, unit: kJ/mol

\( \Delta H_{\text{fluid}} \) heat generated in the fluid during the evaporation process, unit: kJ

\( \Delta \hat{H}_V \) heat of vaporization for water at 100°C, unit: kJ/mol

\( I \) current through the circuit, unit: A

\( I_{\text{arc}} \) current in arc regime, unit: A

\( I_{\text{glow}} \) current in glow regime, unit: A

\( I_{\text{spark}} \) current in spark regime, unit: A
\( j \) emission current density, unit: A/m\(^2\)

\( j_i \) mass flux vector, unit: kg/(m\(^2\)·sec)

\( k \) reaction rate constant, unit: sec\(^{-1}\)

\( k_0 \) pre-exponential factor, unit: sec\(^{-1}\)

\( k_B \) Boltzmann constant, \( k_B = 1.38 \times 10^{-23} \) J/K

\( k_{\text{new}} \) new reaction rate constant calculated through numerical optimization, unit: sec\(^{-1}\)

\( l \) length of the evaporator, unit: m

\( L \) length of the reaction channel, unit: mm

\( m \) number of peak area measurements, unit: dimensionless

\( m_e \) mass of the electron, unit: kg

\( m_{\text{mixture}} \) mass of the mixture of CO\(_2\) and water, unit: kg

\( m_{\text{tube}} \) mass of the tube, unit: kg

\( \dot{m} \) mass flow rate, unit: kg/sec

\( \dot{m}_{\text{in}} \) mass flow rate at the inlet, unit: kg/sec

\( \dot{m}_{\text{out}} \) mass flow rate at the outlet, unit: kg/sec

\( \dot{m}_{\text{products}} \) mass flow rate for the products, unit: kg/sec

\( \dot{m}_{\text{reactants}} \) mass flow rate for the reactants, unit: kg/sec

\( M \) Mach number, unit: dimensionless

\( M_i \) molar mass of component \( i \), unit: g/mol

\( M_k \) molar mass of component \( k \), unit: g/mol

\( M_n \) average molar mass of the mixture, unit: g/mol
\( n \) kinetic parameter that decides the production pathway to CO or CH\(_4\), unit: dimensionless

\( n_c \) number of corona points, unit: dimensionless

\( n_{CO_2} \) mole of CO\(_2\) in the evaporator, unit: mol

\( n_{\text{fluid}} \) mole of the fluid, unit: mol

\( n_{H_2O} \) mole of H\(_2\)O in the evaporator, unit: mol

\( N \) number of pins on the needle plate, unit: dimensionless

\( \dot{n}_m \) molar flow rate of fluid, unit: mol/sec

\( p \) pressure, unit: Pa (unless specified otherwise)

\( P_0 \) pressure at the inlet, unit: Pa

\( P_1 \) startup power, unit: W

\( P_2 \) operation power, unit: W

\( P_{\text{fluid}} \) startup power on fluid, unit: W

\( P'_{\text{fluid}} \) operation power on fluid, unit: W

\( P_L \) pressure at the outlet, unit: Pa

\( P_{\text{tube}} \) startup power on tube, unit: W

\( \frac{\Delta P}{\rho} \) change of pressure drop, unit: J/kg

\( Q \) calculated Q value for Dixon test, unit: dimensionless

\( Q_{\text{table}} \) Q value in the Dixon test table, unit: dimensionless
\( \dot{Q} \)  heat interaction between system and environment, unit: J/sec

differential resistance, unit: \( \Omega \)

\( r \)  radius of needle, unit: mm

\( R \)  gas constant, \( R = 8.314 \text{J/(K\cdot mol)} \)

\( R_0 \)  a quantum mechanical coefficient describing the reflection of electrons from the potential barrier related to the metal surface, unit: dimensionless

\( R^2 \)  coefficient of determination, unit: dimensionless

\( Re \)  Reynolds number, unit: dimensionless

\( R_i \)  reaction rate of component \( i \), unit: \( \text{mol/(m}^3\text{\cdot sec)} \)

\( SE \)  standard error, unit: dimensionless

\( sens \)  sensitivity, unit: dimensionless

\( SS_{res} \)  sum of squares for the residuals, unit: \( \text{(mV\cdot sec)}^2 \)

\( SS_{total} \)  overall variability of the data, unit: \( \text{(mV\cdot sec)}^2 \)

\( t \)  heating time during the evaporation process, unit: min

\( t_{electron} \)  time that activated electrons travel through the gap, unit: sec

\( T \)  final temperature for evaporator and reactor, unit: \( ^{\circ}\text{C} \)

\( T_0 \)  1/1000 of the specified temperature of a compound, unit: K

\( T_1 \)  initial temperature for evaporation process, unit: \( ^{\circ}\text{C} \)

\( T_2 \)  boiling temperature of water, \( T_2 = 100^{\circ}\text{C} \)

\( T_e \)  temperature of the metal, unit: K

\( T_f \)  temperature of the fluid, unit: K

\( TolFun \)  Tolerance of the function, unit: \( \text{(mol/m}^3\text{)}^2 \)
**TolX**  
Tolerance of the variable, unit: sec⁻¹

**TP**  
true positive test results, unit: dimensionless

**ΔT**  
temperature change during the evaporation process, unit: °C

\( \frac{Δ\mu^2}{2} \)  
change of velocity profile, unit: J/kg

**v**  
average velocity of the fluid flow, unit: m/sec

**v_x**  
velocity along the x direction, unit: m/sec

**v_y**  
velocity along the y direction, unit: m/sec

**v_z**  
velocity along the z direction, unit: m/sec

**V**  
voltage applied across the reactor, unit: V

**V_{active}**  
active volume for reaction, unit: mm³

**V_{arc}**  
voltage in arc regime, unit: V

**V_b**  
breakdown voltage, unit: V

**V_{glow}**  
voltage in glow regime, unit: V

**V_{fluid}**  
volume of the fluid in the evaporator, unit: m³

**V_{spark}**  
voltage in spark regime, unit: V

**V_{tube}**  
volume of the stainless steel tube in evaporator, unit: m³

**V_{whole}**  
volume of the whole reaction channel, unit: mm³

**V_{whole,after}**  
volume of the reaction channel after the improvement, unit: mm³

**V_{whole,before}**  
volume of the reaction channel before the improvement, unit: mm³
\( \dot{V} \) volumetric flow rate of the fluid, unit: ml/min

\( w \) range between the maximum and minimum peak areas, unit: mV·sec

\( w_i \) mass fraction of component \( i \), unit: dimensionless

\( W \) width of the reaction channel, unit: mm

\( W_0 \) work function not perturbed by external electric field, unit: eV

\( W_f \) work function of the metal, which is the energy distance from the highest electronic level in metal (the Fermi level) to the continuum, unit: eV

\( W_i \) weight factor in objective function, unit: dimensionless

\( \dot{W} \) work interaction between system and environment, unit: J/sec

\( x_1 \) molar fraction of CO\(_2\) in the fluid, unit: dimensionless

\( x_2 \) molar fraction of water in the fluid, unit: dimensionless

\( x_k \) mole fraction of component \( k \), unit: dimensionless

\( \alpha \) first Townsend coefficient, unit: mm\(^{-1}\)

\( \beta \) exponential kinetic parameter, unit: dimensionless

\( \gamma_{se} \) secondary electron emission coefficient at the cathode, unit: dimensionless

\( \varepsilon \) maximum energy of attraction, unit: J

\( \varepsilon_F \) Fermi energy of metal, unit: eV

\( \eta \) energy efficiency of the microreactor, unit: dimensionless

\( \lambda \) reactor efficiency of the microreactor, unit: dimensionless

\( \mu \) viscosity of the flow, unit: Pa·sec

\( \rho \) density of the flow, unit: g/cm\(^3\)
\( \rho_{\text{tube}} \)  
- density of the stainless steel tube in evaporator, unit: g/cm\(^3\)

\( \sigma \)  
- standard deviation, unit: dimensionless

\( \sigma_m \)  
- standard error, unit: dimensionless

\( \phi \)  
- active volume ratio of the reactor, unit: dimensionless

\( \phi_{\text{before}} \)  
- active volume ratio of the reactor before improvement, unit: dimensionless

\( \phi_{\text{after}} \)  
- active volume ratio of the reactor after improvement, unit: dimensionless

\( \sigma_{ik} \)  
- binary collision diameter parameters, unit: Å

\( \Omega \)  
- collision integral, unit: \( K \), which is the function of reduced temperature \( k_BT/\varepsilon \).
Chapter 1- Introduction

1.1 Introduction and Background

Global warming caused by the emission of greenhouse gases has created extremely negative environmental impacts, such as the rise of sea level, the disappearance of lakes and rivers, and melting of the ice caps. Among various greenhouse gases, carbon dioxide (CO\textsubscript{2}) is considered as the most important one, because of its greenhouse properties and continuous accumulation in the atmosphere.\textsuperscript{1, 2} According to the measurements from NOAA/Earth System Research Laboratory, carbon dioxide currently constitutes about 0.04% (400.83 parts per million) of the atmosphere, which is the highest in the past 57 years (see Figure 1).\textsuperscript{3}

![Atmospheric CO\textsubscript{2} at Mauna Loa Observatory](image-url)

Figure 1. Trend of CO\textsubscript{2} Concentration in the Atmosphere between 1958 and 2015 (Red Line: Measured Data of CO\textsubscript{2} Concentration; Black Line: Seasonally Corrected Data)\textsuperscript{3}
Indeed, human activities cause the increasing concentration of carbon dioxide both by adding more CO\textsubscript{2} to the atmosphere and by influencing the ability of natural sink, like forests, to remove CO\textsubscript{2} from the air. Figure 2 illustrates the status of carbon dioxide emissions for all the countries in the world, and all the larger countries contribute a large proportion of CO\textsubscript{2} emission (see Table 1).\textsuperscript{4} In 2013, CO\textsubscript{2} accounted for about 82\% of all U.S. greenhouse gas emissions from human activities, which include generation of electricity, transportation, and industrial, residential and commercial activities.\textsuperscript{5} Several financial incentives have been implemented, including carbon taxes to reduce the CO\textsubscript{2} emission.

Figure 2. Countries by Carbon Dioxide Emissions in Thousands of Tons per Annum via the Burning of Fossil Fuel in 2010\textsuperscript{4}
Table 1. List of Top Countries by Carbon Dioxide Emissions in Thousands of Tons per Annum via the Burning of Fossil Fuel in 2010

<table>
<thead>
<tr>
<th>Countries</th>
<th>Annual CO₂ Emission (kilotons)</th>
<th>Percentage of World Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>8286892</td>
<td>24.65%</td>
</tr>
<tr>
<td>United States</td>
<td>5433057</td>
<td>16.16%</td>
</tr>
<tr>
<td>India</td>
<td>2008823</td>
<td>5.98%</td>
</tr>
<tr>
<td>Russia</td>
<td>1740776</td>
<td>5.18%</td>
</tr>
<tr>
<td>Japan</td>
<td>1170715</td>
<td>3.48%</td>
</tr>
<tr>
<td>Germany</td>
<td>745384</td>
<td>2.22%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>19385647</strong></td>
<td><strong>57.67%</strong></td>
</tr>
</tbody>
</table>

Carbon Tax is a kind of tax levied on the carbon content of fuels, and it is a form of social cost added to the industrial operation. This policy indirectly encourages the use of renewable energy sources (like sunlight, wind, nuclear and hydropower) rather than hydrocarbon fuel (coal, petroleum, and natural gas). It offers a potentially cost-effective means of reducing greenhouse gas emissions. Some countries have implemented carbon taxes or energy taxes that are related to carbon emission during the production cycle. Although there is no nationwide carbon tax levied in the United States, a few states and localities (such Colorado, California and Maryland) have introduced the tax. Figure 3 illustrates estimated the effect of a carbon tax on the distribution of sources for United States electrical generation. Table 2 estimates the carbon taxes by multiplying carbon dioxide production of the fuel source per unit mass or volume by the Social Cost Carbon. Social Coast Carbon (abbreviation: SCC), is an estimate of the economic damages associated with a small increase in carbon dioxide (CO₂) emissions, conventionally one metric ton, in a given year.
Figure 3. Estimated Effect of an Increasing Carbon Tax on the Distribution of Energy Sources for United States Electrical Generation

Table 2. Estimation of Carbon Taxes based on Various Fuel Sources

<table>
<thead>
<tr>
<th>Fuel</th>
<th>CO₂ Emissions (mass of CO₂ produced per fuel unit)</th>
<th>Tax per m³ of fuel ($)</th>
<th>CO₂ Emissions for Electricity Generation (g/kWh)</th>
<th>Tax per kWh of electricity ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gasoline</td>
<td>2.35 kg/L</td>
<td>28</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>diesel fuel</td>
<td>2.67 kg/L</td>
<td>32</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>jet fuel</td>
<td>2.65 kg/L</td>
<td>32</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>natural gas</td>
<td>1.93 kg/m³</td>
<td>0.023</td>
<td>181</td>
<td>0.0066</td>
</tr>
<tr>
<td>coal (lignite)</td>
<td>1.396 kg/kg</td>
<td>n/a</td>
<td>333</td>
<td>0.0121</td>
</tr>
<tr>
<td>coal (subbituminous)</td>
<td>1.858 kg/kg</td>
<td>n/a</td>
<td>330</td>
<td>0.0119</td>
</tr>
<tr>
<td>coal (butuminous)</td>
<td>2.466 kg/kg</td>
<td>n/a</td>
<td>317</td>
<td>0.0115</td>
</tr>
<tr>
<td>coal (anthracite)</td>
<td>2.843 kg/kg</td>
<td>n/a</td>
<td>351</td>
<td>0.0127</td>
</tr>
</tbody>
</table>
1.2 Sustainable Concept of CO₂ Utilization

Based on the previous discussion in “Introduction” section, it is reasonable that the utilization of CO₂ to produce value added products such as chemical products is an opportunity with growing benefits. The motivations for producing chemicals from CO₂ are listed below:

- In addition that the resource is truly renewable and cheap, CO₂ utilization also reduces to carbon tax liability;
- CO₂ is considered as a nontoxic feedstock that can replace toxic chemicals such as phosgene (which causes severe respiratory effects in humans via acute inhalation exposure)¹¹ and isocyanates (which are dangerous irritants to the eyes and respiratory tract)¹²;
- The successful development of an efficient system producing chemical products employing CO₂ could open new avenues to resource utilization rather than simple storage through sequestration;¹³
- The production of chemicals from CO₂ has a positive impact on the global carbon balance;
- The use of CO₂ as feedstock or co-reactant is an opportunity, which stimulates new approaches in industrial chemistry.¹⁴

However, the barriers and challenges for promoting CO₂ utilization also exist. The primary problem is the control of CO₂ emission. The economic development in the U.S. has benefited greatly from relatively cheap energy sources. Therefore, the idea of regulation of CO₂ emissions by ratifying Kyoto Protocol has not been popular in the United States. Apart from this challenge, the difficulties and barriers for CO₂ conversion and utilization are primarily due to the lack of value-based driving forces, as outlined below:

- Costs of CO₂ capture, separation, purification, and transportation to user site;
- Energy requirements of CO₂ chemical conversion (plus source and cost of co-reactants if involved);
Market size limitations, little investment incentives and lack of industrial commitments for enhancing CO₂-based chemicals;
Lack of socio-economical driving forces for enhanced CO₂ utilization.¹⁵

Accordingly, the strategic objectives of CO₂ conversion and utilization should be based on the unique physical and chemical properties and could include one or more of the broadly defined targets listed below, which will be further elaborated in subsequent sections:

- Use CO₂ for environmentally benign physical and chemical processing that adds value to the process.
- Use CO₂ to produce industrially useful chemicals that increase the value to the products.
- Use CO₂ as a beneficial fluid for processing or as a medium for energy recovery, contaminant removal, and emission reduction.
- Use CO₂ recycling involving renewable sources of energy such as biomass and solar energy or ‘waste’ energy to conserve carbon resources for sustainable development.¹⁵

Listed below are some strategic considerations for developing technologies for CO₂ conversion and utilization:

- To produce useful chemicals and materials using CO₂ as a co-reactant or co-feed;
- To make use of CO₂ based on the unique physical or chemical properties of CO₂;
- To replace a hazardous or less-effective substance in existing processes with CO₂ as an alternate medium or solvent or co-reactant or a combination of them;
- To use CO₂ for energy recovery while reducing its emissions to the atmosphere by sequestration;
- To recycle CO₂ as C-source for chemicals and fuels;
- To convert CO₂ under geologic formation conditions into "new fossil" energies to avoid land and ocean CO₂ emission.¹⁶

Currently, several primary technical approaches for CO₂ utilization have been reported in
the literature, including several chemical methods, like biological,\textsuperscript{17} electrochemical and electrical related,\textsuperscript{18, 19} thermochemical\textsuperscript{20} and photochemical\textsuperscript{21}. Among these methods, electrochemical and electrical related reduction of CO\textsubscript{2} has the highest efficiency and the absent of disadvantages of consuming valuable food resources (biological method) and operating under high temperature (thermochemical process).\textsuperscript{22} The only drawback is the consumption of non-renewable energy, but this can be solved by converting renewable energy into electricity. In this study, the power eventually comes from the solar energy converted using Photovoltaic (PV) panels, which prevents the introducing of more CO\textsubscript{2} into the system.

1.3 Thesis Goal and Objectives

1.3.1 Thesis Goal

The overall goal of this dissertation is:

- To evaluate the feasibility of microscale-based technology for gaseous phase CO\textsubscript{2} reduction process with the present of multi-point corona discharge
- To establish the intrinsic chemical reaction kinetic parameters pertinent to the characterization of multi-point corona discharge chemical reaction process

1.3.2 Objectives

The following objectives would be explored to achieve the goals of this work:

1. Design, fabrication and testing of the Corona Microreactor for CO\textsubscript{2} conversion into chemical products
2. Design, fabrication and assembly of a balance of plant, which will support the operation of microreactor for CO\textsubscript{2} conversion
3. Demonstration of the performance envelope (variations of concentration, P, T, flow rates, etc.) of the Corona Microreactor system under steady state conditions;
4. Development of a mathematical model and numerical simulation of the operation of the Corona Microreactor
(5) Development of the energy model for the chemical process of the corona microreactor and investigation of parameters that determine the energy efficiency of the reactor.

References


Chapter 2- Fundamentals

2.1 Fundamentals of Plasma and Corona Discharge

Plasmas, as tools in the field of chemistry and engineering, provide three major features useful for applications:

(1) Temperatures of at least some plasma components and energy density can significantly exceed those in conventional processes;

(2) Plasmas can create high concentrations of activated or excited species, such as electrons, ions, atoms, radicals, excited states, and photons;

(3) Plasmas can operate far from thermodynamic and chemical equilibrium, allowing for the existence of excited states and activated species and keeping the bulk temperature around room temperature.

The temperature in plasmas is determined by the average energy of the plasma particles and their relative degrees of freedom (i.e. translational, rotational, vibrational and electronic excitations). Plasma is a multi-component system as a mixture of electrons, ions, and excited and neutral species. Each of these separated species can exhibit their characteristic temperatures. In electrically generated plasmas, the energy is firstly accumulated by electrons and then transferred to heavier particles through collisions. The temperature difference between electrons and heavy particles is characterized by the square of the ratio of the electric field to the pressure, \((E/p)^2\). At a small value of \((E/p)^2\), the temperature of massive particles approached the temperature of electrons, and local thermodynamic equilibrium will be created. The plasma at local thermodynamic equilibrium can be characterized by a single temperature. Ionization and chemical processes are determined by this temperature, and the quasi-equilibrium plasma of this kind is referred to thermal plasma or “hot” plasma. When plasma does not have enough energy or time for temperatures of electrons and heavy particles to equilibrate through joule heating, this kind of plasma is usually called non-thermal plasma, or “cold” plasma.

As mentioned above, thermal plasma has electrons and heavy particles in thermal
equilibrium. In other words, they are nearly at the same temperature. However, in non-thermal plasma, the electron temperature often far exceeds the temperature of ions and neutral particles, and as a result, the ionization and chemical processes are determined by the electron temperature in non-thermal plasma.\(^{24}\) Also, due to the higher electron temperature in the non-thermal plasma, the electron vibration is greater, and the light frequency is higher than those in thermal plasmas. That’s the reason why the color of thermal plasma is usually brighter than the color of the non-thermal plasma.\(^{25}\)

When discussing electrically-generated plasmas, these include spark discharge, arc discharge, corona discharge, and dielectric barrier discharge (DBD). Thermal plasmas, including spark and arc discharge, are typically spatially narrow and expend much energy heating the media that they discharge through. The non-thermal plasmas, such as corona discharge and DBD, usually occupy larger volumes in the discharge media and do not intensely heat the surrounding fluid.

Corona discharge is the traditional example of atmospheric pressure, non-thermal plasma and has been used in many industrial applications, such as electrostatic precipitation, electrophotography, static control in semiconductor manufacturing, ionization instrumentation, destruction of toxic compounds, generation of ozone, materials synthesis and modification, chemical synthesis and so on. The behavior of corona discharge highly depends on the geometry of the electrode system, and it can only be formed in highly non-uniform electric fields. This geometry includes the relative size and shape of the electrodes, in addition to the spacing between each electrode. In addition to effects associated with electrode geometry, electrode material and the micro/nanostructure of the electrode play a large part in the specifics of electric breakdown and the properties of the discharge.\(^{26}\)

The major differences between corona discharge and dielectric barrier discharge are represented in the following perspectives:\(^{27}\)

(1) Configuration: The electrode system for dielectric barrier discharge has a dielectric barrier layer between two electrodes (see Figure 4), but for corona discharge to occur the system only has two electrodes and the electric field has to be non-uniform (see Figure
5). Besides, the behavior of dielectric barrier discharge is not related to the geometry of the electrode system.

(2) Current type: dielectric barrier discharge needs to be operated on alternating current (AC) with a frequency of 1 kHz to 10 MHz while corona discharge can only work in DC. Dielectric barrier discharge can be initiated when the applied alternating voltage is higher than the breakdown voltage and sustained by the driving oscillation of charges accumulated through dielectric barrier layer(s). However, if an alternating voltage applied between the two conductive electrodes, both electrodes will alternately act as the anode and cathode. In this case, the accumulated charges during one half-cycle will be neutralized by the opposite charge accumulated during the next half-cycle. That’s the reason corona discharge cannot be generated in AC.

Figure 4. Basic Dielectric-Barrier Discharge Configurations

Figure 5. Basic Corona Discharge Configurations
According to Figure 5, there are several configurations for corona discharge. In this study of CO\textsubscript{2} reduction, the configuration of point-to-plane (configuration d in Figure 5) is applied. The structure of point-to-plane corona discharge can be divided into two regions: ionization region and drift region. Ionization region is the high field around the active electrode where gas ionization process occurs, and drift region is the low field connecting the ionization region with the eventual low field, passive electrodes. Positive and negative corona discharges have different structures as shown in Figure 6. The corona geometry is named positive, negative, bipolar, AC or HF, according to the polarity of the active electrode(s), but all discharge forms have ionization regions, and the distinguishing feature of coronas is the drift region. In unipolar conduction coronas, the drifting ions or electrons will always be of the corona polarity and their space charge field will be the dominating factor in determining both the corona I-V characteristic and the current density distribution in the discharge gap. The negative corona has a much greater electron density and needs lower energy to ignite, which it’s more energy efficient.\textsuperscript{29}

![Diagram of corona discharge]

**Figure 6. Structures of point-to-plane corona with ionization region and drift region (a: positive; b: negative)\textsuperscript{30}**

The representative voltage-current relationship for negative plasmas is shown below in Figure 7. Although this V-I curve is generated for the particular needle-to-plane configuration and only generally representative, it is a useful tool in understanding how electrically generated plasma behave in different operating regimes of plasma.
Figure 7. Representative V-I Relation in Negative DC Voltage Applied to the Needle-to-plane System\textsuperscript{31}

The transition procedure of the negative corona (Figure 7) is described as below,\textsuperscript{31, 32} and the phenomena of discharges in different regimes are illustrated in Figure 8:

1. The lowest current regime is called **dark regime** (or **Townsend regime**), which is composed of Townsend discharge. Townsend discharge is a gas ionization process where free electrons accelerated by a sufficiently strong electric field give rise to electrical conduction through a gas by avalanche multiplication caused by the ionization of molecules by ion impact. When the number of free charges drops or the electric field weakens, the phenomenon ceases.

2. The next region with a higher current density is **spark regime**. Uniformly repetitive pulses appear in this section. These pulses can absorb electrons to form low mobility negative ions, and they are called Trichel pulses. Trichel pulses are generated because of secondary electron emission.\textsuperscript{33} Trichel pulses only occur in electronegative gasses, which have an affinity for electrons, because it requires negative particles for triggering pulses.\textsuperscript{34} Since air has a higher electronegativity than CO\textsubscript{2}, discharges in CO\textsubscript{2} are more...
continuous than those in the air.\(^{35}\)

(3) After the current density is increased further, **glow regime** (or **corona regime**) is reached. In this regime, the entire gap is full of negative ions. A pulseless discharge bridges the gap with a gentle glow. In the air, the glow is in purple, while the glow is in bluish white in CO\(_2\).

(4) The section with the highest current density is called **arc regime**. In this regime, the pulseless discharge in the last regime evolves into thermally intense plasma with a bright glare.

![Figure 8. Discharges in Different Regimes (Upper left: dark regime, invisible discharge; Upper right: spark regime, pulsed discharge; Bottom left: glow regime, continuous discharge with gentle glow; Bottom right: arc regime, thermal intense discharge with bright glare)](image)

The breakdown voltage between two electrodes in gasses is the voltage necessary to start a discharge or electric arc. Paschen’s law is an equation to predict the breakdown voltage as a function of pressure and gap length. **Figure 9** demonstrates plots of Paschen’s law equation for some gasses.
Figure 9. Plot of Paschen’s Law Equation for Several Gases

\[
\frac{\alpha}{p} = A \exp \left( - \frac{Bpd}{V_b} \right) \Rightarrow V_b = \frac{B(pd)}{\ln[A(pd)] - \ln[\ln(1+1/\gamma_{se})]} \\
\alpha d = \ln \left( 1 + \frac{1}{\gamma_{se}} \right)
\]  \hspace{1cm} (Eq. 2-1)

where \( V_b \) is the breakdown voltage, unit: Volts, and it has a minimum when \( Apd = \ln(1+1/\gamma_{se}) \);

\( p \) is the pressure, unit: Torr;

\( d \) is the gap distance between electrodes, unit: mm;

\( \alpha \) is called first Townsend coefficient, unit: mm\(^{-1}\);

\( \gamma_{se} \) is called secondary electron emission coefficient at the cathode;

\( A \) is the saturation ionization constant for the gas at a particular \( E/p \) (electric field/pressure), unit: (Torr·mm\(^{-1}\));

\( B \) is a constant related to the excitation and ionization energies, unit: V·(Torr·mm\(^{-1}\)).

From the V-I curves above, it can be found that the current decreases as the voltage increases in part of the curves (See Eq. 2-2), which illustrates that plasma is a negative
differential resistance (NDR) load.

\[ r_{\text{diff}} = \frac{dv}{di} < 0 \]  
(Eq. 2-2)

The V-I curve is non-monotonic with regions of negative slope representing negative differential resistance. Negative differential resistance can be classified into two types: voltage controlled negative resistance (VCNR) and current controlled negative resistance (CCNR), as shown below in Figure 10. Plasma is a current controlled negative resistance. Therefore, the way to control the conditions of corona reactor is to set the voltage equal or higher than the maximum voltage \( V \geq V_2 \) and then change the current to obtain the aimed operation spot.³⁷

![Figure 10. I-V curves for two kinds of negative differential resistance (Left: voltage control; Right: current control)](image)

2.2 Transport Phenomena in Microscale-based Structures

Microtechnology can be described as the study, development, and application of devices whose operation is based on the scale of 1-100 microns. The widely accepted term “microreactors” in this technology is usually defined as miniaturized reaction systems fabricated by using, at least partially, methods of microtechnology and precision engineering. The characteristic dimensions of the internal structures of microreactors like fluid channel typically range from the sub-micrometer to the sub-millimeter level. The construction of microreactors is performed in a hierarchic manner, comprising an
assembly of units composed of subunits and so forth.\textsuperscript{38}

Originating from chemical engineering principles, four fundamental advantages associated with miniaturized reaction vessels make microreactors more favorable than traditional systems. The combination of these four benefits forms the sweet spot of the microreactors, as shown in Figure 11.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{sweet_spot_microreactors}
\caption{Sweet Spot of the Microreactors}
\end{figure}

(1) Advantages Arising from Fundamental Phenomena

Intensification of Heat and Mass Transport

Due to short diffusional distances, the driving forces for heat and mass transfer can be significantly enhanced in microsystems for any diffusion-limited process. According to Fick’s law and Fourier’s law, as shown below, for a given chemical process, decreasing diffusion distance by a factor of \( n \) will result in the increases of mass flow rate and heat flow rate respective by \( n^2 \) and \( n \). This theoretical prediction was exemplarily verified by a number of studies.\textsuperscript{39-41}

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]  
(Eq. 2-3)
Fourier’s law: \[ \frac{\partial Q}{\partial t} = -kA \frac{\partial T}{\partial x} \] (Eq. 2-4)

Reduced Size

Due to the reduction of the linear dimensions, the volume of microreactors is significantly decreased compared to conventional large-scale reactors. Hardware mass can also be reduced by 5-50 times. Reduction of the size also contributes to shifting size-energy trade-offs toward higher efficiency.

Large Surface to Volume Ratio

As a consequence of the decrease in fluid layer thickness, the corresponding surface-to-volume ratio of the fluid entity is also notably increased. Specific surfaces of microchannels amount to 10,000 to 50,000 m\(^2\)/m\(^3\), whereas typical laboratory and production vessels usually do not exceed 1000 m\(^2\)/m\(^3\). This increase not only benefits to heat transfer but also can be utilized for catalytic reactors because of more chance of interaction between reactants and catalyst.

Other benefits arising from fundamental phenomena include changing chemical product distribution, lowering pressure drop, gravity independence, a high degree of reaction control, extremely high quench rates, etc.

(2) Advantages Arising from Parallel Architecture

Production Flexibility

Rather than by scaling-up, an increase in throughput in microreactors is achieved by a numbering-up approach. The functional unit of a microreactor is multiply repeated. The fluid connection between these units can be achieved by using distribution lines and flow equipartition zones, most likely hierarchically assembled. This numbering-up strategy results in higher flexibility in adapting production rate to varying demand since a certain number of systems can be switched off, or further systems may be directly added to the production plant without influence on other components. A plant design based on a large number of small reaction system can be modified to perform a variety of reactions by changing the piping network. This flexibility may be supported by a considerably broader
range of operating conditions of a microreactor compared with a macroscopic system.

**Operating Robustness and Controllability**

The numbering-up approach mentioned above also allows problems to be isolated and repaired. Compared with shutting down the whole device to solve problems in the conventional system, microreactor is more controllable and powerful.

(3) Advantages Arising from Commercial Applications

Due to reduced size of reactors, less space, materials and energy are required for microreactors, and operation time can be reduced to seconds, milliseconds, in some cases even nanoseconds. These result in lower capital investment, operating cost and cost of transportation of material and energy to be consumed. In addition, the numbering-up strategy allows simple and inexpensive replication of microreactor units, and avoids complexity and intensively increasing cost of large-scale production. Besides, techniques like replacing batch with continuous processes, distributed production and integration of microtechnology with other systems can be applied to reduce the contact time, which also contribute to lowering the cost.

(4) Advantages in the Area of Safety and Security

Until recently, highly exothermic chemical reactions, involved the use of relatively large volume conventional processing equipment, still have a high possibility of fires or explosion. The primary reason of this is the inability to extract the heat generated by the reaction due to the small ratio of the surface area of the chamber walls to the material volume. However, microreactors composed of narrow channels have a larger surface-to-volume ratio and little volume, which can have better control over temperature and other process conditions and can translate to lower stored energy. Besides, due to the small volume, fewer amounts of reactants and products can guarantee the safety of the process. Even though a microreactor fails, a few chemicals accidentally released could be easily contained. All the features above illustrate that microreactors are promising devices for safe operations in manufacturing.

In this study of DC corona microreactor, the electrode gap required to access certain
desirable plasma states at atmospheric pressure is only possible at sub-millimeter separation. It means that microscale is the only reactor size suitable for the scale of corona discharge. Microtechnology is necessary to control the energy density of plasmas, and it can result in new possibilities for controlling the chemical product type and yield of the reactor.

2.3 Kinetics and Thermodynamics of Chemical Reactions in Corona Discharge

The negative-polarity, direct-current corona discharge process in a point-to-plane geometry is illustrated below in Figure 12. The sketch is not to scale; the corona plasma region occupies only a fraction of the interelectrode spacing. The plasma region is defined as the area in which electron-impact reactions are likely to occur. The boundary is arbitrary selected here as the radius where the reduced electric field (E/N) is 80 Td, corresponding to a mean kinetic energy of electrons equal to 1.85 eV. Here, E/N is the ratio between electric field (E) and concentration (N) of neutral particles. Townsend (symbol Td) is a physical unit of the reduced field (1 Td = $10^{-21}$ V·m$^{-2}$).

![Figure 12. Sketch of a Self-sustained Negative DC Corona Discharge](image)

Negative corona is only possible in electronegative gasses, such as oxygen, water vapor,
and carbon dioxide. A negative high voltage is applied to the pointy electrode, and the plane is grounded. The corona discharge is initiated when the electric field near the pointy electrode is sufficient to ionize the gaseous species. Seed electrons to initiate the ionization process are produced by naturally occurring ionization events. The free electrons generated in the initial ionization process are accelerated away from the pointy electrode in the imposed electric field. Inelastic collisions of electrons and neutral gas molecules produce more electron-positive ion pairs in a self-sustained process referred to as the electron avalanche.\textsuperscript{43, 44} Secondary electrons to sustain the discharge may be generated by photoemission from the pointy discharge electrode, bombardment of the discharge surface by positive ions, or photoionization in the gas.\textsuperscript{45} The mean kinetic energy of ions in the corona plasma is on the order of 0.01-0.1 eV. These ions are not energetic enough to knock out electrons from the electrode, but the short-wavelength photons emitted in the corona discharge are energetic enough to either ionize the gaseous species or to extract electrons from the electrode surface. Because the work required to remove electrons from the electrode surface because of thermionic emission, which is approximately 4\textendash{}5 eV for the metal electrodes,\textsuperscript{46} is considerably less than the ionization energy of carbon dioxide and water vapor, the yield of photoelectrons from the electrode surface is much higher than that from the gas. Therefore, the most significant mechanism for the generation of the secondary electrons is photoemission from the pointy discharge electrode.\textsuperscript{42}

Thermionic emission mentioned in the previous paragraph refers to the phenomena of electron emission from a high-temperature metal surface (e.g., hot cathode), which is due to thermal energy of electrons located in metal. Emitted electrons can remain in the surface vicinity creating there a negative space charge, which prevents further electron emission. However, the electric field in the cathode vicinity is enough to push the negative space charge out of the electrode and reach the saturation current density.\textsuperscript{24}

The Sommerfeld formula describes the emission current density $j$ for thermionic emission:
\[ j = \frac{4\pi m_e e}{(2\pi h)^3} T_e^2 (1 - R_0) \exp \left( -\frac{W_f}{T_e} \right) \]  

(Eq. 2-5)

Where \( m_e \) is the mass of an electron, unit: kg;

\( e \) is the charge of an electron, unit: Coulomb;

\( h \) is Planck’s constant, unit: J·sec;

\( T_e \) is the temperature of the metal, unit: K;

\( R_0 \) is a quantum mechanical coefficient describing the reflection of electrons from the potential barrier related to the metal surface, unit: dimensionless;

\( W_f \) is the work function of the metal, which is the energy distance from the highest electronic level in metal (the Fermi level) to the continuum, unit: eV. It corresponds to the minimum energy necessary to extract an electron from the metal, and it depends on radius and charge of particles.\(^{24} \)

According to the Sommerfeld formula, the emission current density increases with increasing temperature, decreasing work function, and growing radius of the tip.

If the external electric fields are very high, the emission current density \( j \) can be described by the Fowler-Nordheim formula:

\[ j = \frac{e^2}{4\pi^2 \hbar} \frac{1}{W_0 + \psi_F} \sqrt{\frac{\psi_F}{W_0}} \exp \left( -\frac{4\sqrt{2mW_0^{3/2}}}{2e\hbar E} \right) \]  

(Eq. 2-6)

Where \( \psi_F \) is the Fermi energy of metal, unit: eV;

\( W_0 \) is the work function not perturbed by external electric field, unit: eV;

\( E \) is the external electric field, unit: V/cm.

Except the thermionic and field emissions, there are some other mechanisms of electron emission from solids to surface bombardment by different particles, and they are called secondary electron emission. Secondary electron emission is a phenomenon where primary incident particles of sufficient energy induce the emission of secondary particles.
when hitting a surface. The secondary electron emission does not make a significant contribution in electrode kinetics of arc discharge but is the principal distinctive feature of the glow discharges. Because of the adiabatic principle, the direct ionization in collisions of ions with neutral atoms is not sufficient. Therefore, ionization cannot be provided through the energy transfer from heavy ions to light electrons. The secondary electron emission induced by ion impact will be necessary in this case. The secondary electron emission is characterized by the coefficient $\gamma_{se}$, which effectively starts growing with very high ion energy while still cannot be negligible at lower ion energy.\(^{24}\)

### 2.4 Energy Consumption in Corona Discharge Chemical Reaction Processes

The basis for any efficiency analysis is through the principles of mass and energy conservation. The mass conservation law indicates that the masses of products and reactants are equal in a chemical reaction. A general steady-state mass rate balance can be expressed as follows:

$$m_{in} = m_{out} \text{ or } m_{reactants} = m_{products} \quad \text{(Eq. 2-7)}$$

The conservation of energy principle applies whether or not a chemical reaction occurs within the system. A general steady-state energy balance can be expressed as follows:

$$\dot{E}_{out} - \dot{E}_{in} = \Delta \dot{E}_{system} = \dot{W} - \dot{Q} \quad \text{(Eq. 2-8)}$$

In (Eq 2-8), $\dot{W}$ represents the work interaction, which can be shown below:

$$\dot{W} = \dot{m} \left( \frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta h + F_{loss} \right) + \dot{E}_{external} \quad \text{(Eq. 2-9)}$$

Since the differences in pressure drop, velocity profile and potential energy and the friction loss can be neglected, the work interaction can be expressed as $\dot{W} = \dot{E}_{external}$. Also, there is no heat interaction between system and environment, $\dot{Q} = 0$.

$$\dot{E}_{out} - \dot{E}_{in} = \dot{E}_{external} \quad \text{(Eq. 2-10)}$$

The energy flow can be expressed as
\[ \dot{E} = \sum_m \dot{n}_m \left( \overline{h}_j^0 - \Delta \tilde{h} \right)_m \]  
(Eq. 2-11)

where \( \dot{n}_m \) is the molar flow rate (unit: mol/s);

\( \overline{h}_j^0 \) is the enthalpy of formation for each species (unit: \( \text{kJ/mol} \)), which can be found in the literature (see Appendix D);\(^{47} \)

\( \Delta \tilde{h} \) is the change of specific enthalpy for each species (unit: \( \text{kJ/mol} \)), which can be evaluated using Shomate equation (Eq 2-12).

\[ \Delta \tilde{h} = AT_0 + B \frac{T_0^2}{2} + C \frac{T_0^3}{3} + D \frac{T_0^4}{4} - E \frac{1}{T_0} + F - H \]  
(Eq. 2-12)

where \( T_0 \) is 1/1000 of the specified temperature (in K) of a compound and \( A, B, C, D, E, F, G \) and \( H \) are constants found in the literature (see Appendix D).\(^{47} \)

The energy efficiency of the microreactor is

\[ \eta = \frac{\dot{E}_{\text{out}} - \dot{E}_{\text{in}}}{\dot{E}_{\text{electrical}}} = \frac{\sum_m \dot{n}_{m,\text{out}} \left( \overline{h}_j^0 - \Delta \tilde{h} \right)_m - \sum_m \dot{n}_{m,\text{in}} \left( \overline{h}_j^0 - \Delta \tilde{h} \right)_m}{V \cdot I} \]  
(Eq. 2-13)

with the remainder lost to the environment as heat.

The reactor efficiency can be expressed as below

\[ \lambda = \phi \eta = \frac{\dot{E}_{\text{out}} - \dot{E}_{\text{in}}}{V \cdot I} \]  
(Eq. 2-14)

where \( \phi \) is the active volume ratio.

References


Chapter 3- Proof-of-concept Experiments for CO₂ Reduction in Microscale-based Corona Reactor

Carbon dioxide (CO₂) is considered as the primary cause of climate change, because of its greenhouse properties and continuous accumulation in the atmosphere. Any success in the research and development of a feasible CO₂ utilization method would signify the achievement of two objectives: (1) to slow down the accumulation of greenhouse gases in the atmosphere; and (2) to provide better carbon resource utilization. However, due to the low energy content of CO₂, a significant amount of additional energy (would, in turn, induce more CO₂ emission) is required for the conventional catalytic reduction of CO₂.⁴⁸

Recently, non-thermal plasma has attracted much attention with regards to the effective and efficient industrial applications. The electrons in non-thermal plasma can reach temperatures of 10⁴~10⁵K (1~10eV) while the gas temperature can remain as low as room temperature. The high electron temperature determines the unusual chemistry of non-thermal plasmas. Based on mechanisms of plasma generation, applied pressure, and electrode geometry, non-thermal plasmas can exist as several different types, including glow discharge, corona discharge, dielectric barrier discharge (DBD), microwave discharge, and radio frequency (RF) discharge.⁴⁹, ⁵⁰ Among these types of non-thermal plasmas, corona discharge is considered as the efficient technique for CO₂ reduction and can be initiated at atmospheric pressure with non-uniform electrode geometry.⁵¹

Ever since non-thermal plasma approach for CO₂ utilization was first summarized in 1999,⁵² excellent progress has been made with a contribution to reducing the atmospheric loading while generating a profit, and these CO₂ utilization processes include CO₂ dissociation, CO₂ reforming, hydrocarbons synthesis from CO₂ and oxygenates synthesis from CO₂.

The dissociation of CO₂ to CO is the simplest and primary reaction for CO₂ reduction. This reaction is kinetically hindered in the conventional process because of the increase of change of Gibbs free energy ($\Delta G_{1000K} = 190.5kJ/mol$), but non-thermal plasma is sufficient to activate the reaction and the primary reaction for all CO₂-involved plasma
reactions is shown below:

\[ \text{CO}_2 \xrightarrow{\text{eq}} \text{CO}^* + O^* \]  

(Eq. 3-1)

Some original investigations have been conducted for the CO\textsubscript{2} dissociation using corona discharge.\textsuperscript{51, 53} Some types of CO\textsubscript{2} adsorbent, such as zeolite, can result in a much higher CO\textsubscript{2} dissociation rate under corona discharge.\textsuperscript{54}

The CO\textsubscript{2} reforming of methane can generate syngas (CO and H\textsubscript{2}), which can be used for higher hydrocarbon formation process, such as Fischer-Tropsch synthesis. However, the conventional reforming reaction has two drawbacks: (i) reaction is endothermic, and it requires a high temperature for a favorable equilibrium (\(\Delta H^\circ = 258.9\text{kJ/mol}\)); (ii) with the present catalyst designs, undesirable carbon deposits are unavoidable. With the application of AC and DC corona discharge at atmospheric pressure, the conversions below 380K are higher than the equilibrium conversions at 890K, thus demonstrating the advantages of plasma chemistry.\textsuperscript{55, 56}

Hydrocarbons synthesis from CO\textsubscript{2} can be mainly divided into two categories: (i) oxidative coupling of CH\textsubscript{4} with CO\textsubscript{2} and (ii) hydrogenation of CO\textsubscript{2}/CO to C\textsubscript{2} hydrocarbons. For case (i), CO\textsubscript{2} can represent a better oxidant than oxygen for the oxidative conversion of methane to higher hydrocarbons, and the typical products are C\textsubscript{2} hydrocarbons, CO, and water. Although the equilibrium yields of C\textsubscript{2} are relatively high, the yield over metal oxide catalysts was not sufficiently high. Also, the oxidative coupling reactions were less-favored thermodynamically compared to the CO\textsubscript{2} reforming of methane. Therefore, gas discharges might offer a good alternative to these conventional catalytic conversions. Zhang et al.\textsuperscript{57} reported using pulsed corona plasma as an activation method for methane reforming with carbon dioxide over the La\textsubscript{2}O\textsubscript{3}/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} catalyst; the product was C\textsubscript{2} hydrocarbons and by-products were CO and H\textsubscript{2}. For case (ii), hydrogenation of CO\textsubscript{2}/CO is a two-stage process: in the first step, the CO\textsubscript{2} decomposition was conducted using a glow discharge in the presence of hydrogen to produce CO; the catalytic hydrogenation of CO was then carried out to produce methane and liquid organic substances in the second step. CO\textsubscript{2} and the dissociated product CO can also be
directly converted to more valuable hydrocarbons using non-thermal plasmas in the absence of a catalyst.\textsuperscript{48}

Several oxygenates can be generated from oxygenates synthesis of CO\textsubscript{2} in the presence of non-thermal plasma, including methanol,\textsuperscript{58, 59} aldehydes\textsuperscript{48} and acetic acid.\textsuperscript{60} However, dielectric barrier discharge is more efficient than corona discharge for this type of reaction.

The discussions above regarding CO\textsubscript{2} utilization in non-thermal plasma are typically on the centimeter or multiple millimeter scales while the performance can be improved in a microreactor system, the scale of which is sub-millimeter or micrometer level. Microreactor systems offer two primary advantages respectively in the fields of reaction engineering and electrical engineering: (i) The use of components and structures on the micro scale creates high gradients on temperature, concentration, pressure and reactive species, which enables rapid heat and mass transfer. The rapid heat and mass transfer are beneficial for chemical reactions, especially those involving fast reaction times and unstable intermediates, and for efficient energy management. Also, the feature of large surface-to-volume ratio benefits the heat transfer and catalytic reactions.\textsuperscript{61} (ii) Plasmas generated within sub-millimeter or micrometer scale, referred to as microplasmas, are characterized by small physical size, high stability of pressure, and high electron density.\textsuperscript{62}

In this study, proof-of-concept experiments were conducted before the design and manufacture of the reaction system to determine the configuration of the reactor: through-liquid and through-gas. After that, a microscale-based corona reaction system was designed, manufactured, constructed and operated for reduction of CO\textsubscript{2} with and without water into more valuable chemical products, such as carbon monoxide (CO) and methane (CH\textsubscript{4}). Two microscale-based corona reactors were designed and built to investigate the effect of active volume ratio.
3.1 Determination of Reactor Configuration

Before the design and manufacture of the micro-based corona reactor, the configuration of the reactor needs to be determined: through-liquid or through-gas. Several experiments were conducted to decide which one is more suitable for CO₂ reduction process.

3.1.1 Through-Liquid Discharges

In this series of experiments of testing through-liquid discharges, ionic liquid BMIM-BF₄ aqueous solution (20% v/v) is chosen as the electrolyte because of the following three reasons. Firstly, most of the ionic liquid have incredibly broad temperature ranges, usually from below ambient to over 300 to 400°C, which allows them to be functional under unique processing conditions. Secondly, most of the ionic liquids have a relatively higher solubility for CO₂ than aqueous system (e.g. the solubility of CO₂ in BMIM-BF₄ is around 30 times than the one in pure water). Finally, some ionic liquid (e.g. EMIM-BF₄ and BMIM-BF₄) can trap CO₂ by forming a molecular complex (EMIM⁺-(CO₂)⁻ and BMIM⁺-(CO₂)⁻), which can lower the potential required to convert CO₂.

1. Electrode plate Configuration

A reactor cell as the one shown in Figure 13 was manufactured. It consists of four parts: polycarbonate top plate, two electrode plates, Teflon substrate and polycarbonate bottom plate. These four components were assembled through screws and alignment holes. The liquid can be filled through the reservoir on the top plate, and both of the electrodes are submerged in it. Two separate electrode plates were attached to the Teflon substrate with four 100-micron slits between triangular shape ladders. The four slits are the locations where the discharges are supposed to occur. Two electrode plates were manufactured using laser cutting while the other three parts of the reactor cell were machined by CNC. Four different materials were used to prepare the electrode plates: graphite, graphite sputtered with gold/palladium, titanium, and nickel. Scheme of electrode plates with triangular shape ladders is shown in Figure 14.
The experimental set-up for electrode plate configuration is illustrated in **Figure 15**. There are five components in the experimental set-up: power supply, reactor cell, ballast resistor, measuring resistor and oscilloscope. The power supply used in this experiment is
a high-voltage DC power supply (current: 0~120mA; voltage: 0~10kV), and ballast resistor with a resistance of 1MΩ and measuring resistor with a resistance of 100kΩ were used. The role of ballast resistor is to protect the power supply and other components in the circuit. An oscilloscope was used to measure the voltages across the reactor cell and measuring resistor respectively. Channel 1 is for the reactor cell, and Channel 2 is for the measuring resistor. The current in the circuit can be calculated with the voltage and resistance of measuring resistor, and plot of voltage across reactor cell versus current can be produced.

Figure 15. Scheme of Experimental Set-up for Electrode-plate Configuration

Figure 16 below illustrates the change of graphite electrode plates along with the increasing power applied across them (from A to C). During this process, bubbles were firstly generated on only the negative electrode and then move to both electrodes, and this phenomenon was more and more intense as the power increases. Also, graphite
electrodes started to disassemble during this process, mainly on the positive electrode. A lot of heat was generated with high voltage applied which vaporized the electrolyte. However, no electrical discharge was observed during this process.

![Figure 16. Change of Graphite Electrode-plates through Increasing Voltage (from A to C) in Ionic Liquid BMIM-BF₄ Aqueous Solution (20% v/v)](image)

The V-I curves in Figure 17 demonstrate that the increasing power tends to develop the current instead of the voltage in ionic liquid solution. This result indicates that increasing the power only increases the number of electrons in the system. The prerequisites of electrical discharge are high voltage and low current, so electrical discharges are absent with such low applied voltages. Although gold/palladium sputtered graphite is better at suppressing the growth of current, it is still not helpful for increasing the voltage to the desired level.
Figure 17. V-I Curves for Graphite and Sputtered Graphite Electrode-plates Configuration in Ionic Liquid BMIM-BF$_4$ Aqueous Solution (20% v/v)

Although electrical discharges cannot be generated in the ionic liquid aqueous solution, reduction of hydrocarbonates can occur in this condition. Figure 18 illustrates the result of gas chromatography for formic acid (HCOOH) reduction reactions. The gas chromatograph used in this study is an SRI 8610C with helium ionization detector (HID). According to the research during my master program, formic acid is the first intermediate generated during the electrochemical CO$_2$ reduction in the liquid phase. Therefore, reduction of formic acid is one step closer to the conversion of CO$_2$. From Figure 18, it can be observed that formaldehyde and methanol are the products of reduction of formic acid.
Above all, it can be concluded that electrical discharge cannot be generated in electrode plate configuration with the presence of ionic liquid solution. There are two possibilities to explain the failure of the generation of electrical discharge: (i) the electric field created by the electrode plate configuration is still too uniform, making it difficult to generate electrical discharge; (ii) ionic liquid BMIM-BF$_4$ is so conductive that not enough electrons contribute to the electrical discharge. To confirm these assumptions, further investigations need to be conducted.

2. Needle-to-needle Configuration

The needle-to-needle configuration was designed for the confirmation of the two assumptions mentioned above: (i) two opposite-positioned needles can create a highly non-uniform electric field; (ii) a less conductive liquid acetonitrile can be used to
compare with the ionic liquid solution.

The experimental set-up for needle-to-needle configuration, illustrated in Figure 19, is similar to the one for electrode plate configuration except that an electrolyte-filled vial replaces the reactor cell with two opposite-positioned needles submerged. The two opposite-positioned needles are respectively stainless steel wire as the anode and tungsten sharp needle as the cathode.

![Power Supply Diagram](image)

**Figure 19. Scheme of Experimental Set-up for Needle-to-needle Configuration**

To form a highly asymmetrical electrode geometry to make it easier for generation of corona discharge, the tungsten needle was manufactured from a tungsten rod using electrolysis etching method to make it sharp. The experimental set-up of this electrolysis etching and photograph of tungsten needle under a microscope are respectively shown in Figure 20 and Figure 21.
Figure 20. Scheme of Experimental Set-up for Tungsten Rod Electrolysis Etching

Figure 21. Photograph of Sharp Tungsten Needle under a Microscope with Dimensions

The procedure of the electrolysis etching is illustrated in Figure 22 and listed below:

1. Cover one end of the tungsten needle rod with tape or wax and the coated part is supposed to be the needle;

2. Submerge a stainless steel wire and the coated part of the tungsten rod into 3mol/L NaOH Aqueous Solution.
NaOH aqueous solution, making sure the liquid level is about 2mm above the covered part;

(3) Connect the stainless steel wire and tungsten rod to the circuit with a power supply and a ballast resistor, making sure the tungsten rod is closer to the positive side of power supply while stainless steel wire is closer to the negative side;

(4) Adjust the voltage to the power supply and resistance of ballast resistor to generate a current of 100~200mA. During the process, bubbles were produced on the stainless steel wire, while the tungsten rod was etched around the liquid level into a biconcave shape because of mass transfer and fluid dynamics. Eventually, when the tungsten bar around the fluid level is thin enough, the gravity will pull down the covered part, which is the desired piece. The electrochemical reactions occurred on cathode and anode are as follows:

Cathode: \( 6H_2O + 6e^- \rightarrow 3H_2(g) + 6OH^- \) \hspace{1cm} (Eq. 3-2)

Anode: \( W(s) + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^- \) \hspace{1cm} (Eq. 3-3)

Overall: \( W(s) + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2(g) \) \hspace{1cm} (Eq. 3-4)

![Diagram](image)

**Figure 22. Procedure of Electrolysis Etching of Tungsten Needle**

As illustrated in **Figure 23**, with the same amount of voltage applied to two needles,
electrical discharge can only be observed in acetonitrile, while in ionic liquid BMIM-BF₄ aqueous liquid nothing was generated across the gap but small gas bubbles appeared on the tungsten needle, which can be due to the splitting of water.

Figure 23. Phenomena at Same Voltage (V_{needles} = 2.0kV) between Two Needles in Ionic Liquid BMIM-BF₄ Aqueous Solution (20% v/v) (A) and Acetonitrile (B)

The two V-I curves in these two different liquids illustrate two entirely different behaviors as the power increases (see Figure 24). Similar to the V-I curves in Figure 17, the V-I curve of ionic liquid in needle-to-needle configuration also indicates that the current develops much faster that voltage as the power increases, while in the V-I curve of acetonitrile the voltage reaches kilovolt level and the symbolic voltage drop appears. This result is due to the significant negative differential resistance developed by the ionization across the entire gap. It is safer to state that ionic liquid is too conductive for the generation of electrical discharge after the comparison of the V-I curves.
Above all, the ionic liquid solution has been proved not suitable for the generation of electrical discharge due to its high electrical conductivity. Although electrical discharge can be generated in some less conductive liquids, such as acetonitrile, these liquids are not helpful for CO$_2$ reduction process because of their low solubility of CO$_2$.

### 3.1.2 Through-Gas Discharge

In this series of experiments of testing through-gas discharges, air and CO$_2$ are chosen as the electrolytes.

1. Electrode-plate Configuration

The structure of the reactor cell and the experimental set-up are the same as shown in Figure 13-15 except the electrolyte is air instead of the ionic liquid solution. Besides
graphite, titanium and nickel have also been chosen as the material for the electrode plate. **Figure 25** below illustrates the phenomena of discharges across three different electrode plates with the same amount of voltage applied. It can be observed that electrical discharges can be generated on all three electrode plates, but they only occurred in one or two gaps simultaneously but jump back and forth among all four gaps. The variance of the gap distances was measured using a microscope, and the variance is around 100µm. It may be too large to keep the discharges stable on all four gaps.

![Figure 25. Phenomena of Discharges at Same Voltage (V_{reactor} = 2.0kV) Across Graphite (A), Titanium (B) and Nickel (C) Electrode Plate in the Air](image)

The V-I curves shown in **Figure 26** all have high voltages at kilovolt level and the typical voltage drop of electrical discharge. They have different breakdown voltages and currents, which is due to the difference of materials of the electrode plates.
Figure 26. V-I Curves of Discharges with Graphite, Titanium and Nickel Electrode Plates in the Air

The experimental results in electrode plate configuration indicate that the electrode plate configuration is asymmetrical enough to generate electrical discharges, and it can occur in the gas phase. However, this configuration has a drawback on controlling the gap distances which can influence the performance of the discharges. To overcome this shortcoming, another two configurations have been designed: needle-to-liquid and needle-to-solid. The only difference between these two is needle-to-liquid has a liquid layer between the needle and metal plate.

2. Needle-to-liquid and Needle-to-solid Configurations

The reactor cell (see Figure 27) for these two configurations has four components: polycarbonate bottom plate, nickel electrode plate, polycarbonate top plate and tungsten needle. The first three elements can be assembled, and liquid can be filled through the reservoir on the top plate for needle-to-liquid. Tungsten needle is manufactured using the electrolysis etching method mentioned above and is fixed around 500µm above the liquid.
surface (needle-to-liquid) or surface of nickel plate (needle-to-solid). The nickel electrode plate is longer than the two polycarbonate plates so the extra area can be used for electrical connection. For needle-to-liquid configuration, ionic liquid BMIM-BF$_4$ aqueous solution (20% v/v) is chosen as the liquid to fill in the reservoir.

**Figure 27. Scheme of Reactor Cell for Needle-to-liquid and Needle-to-solid Configurations**

As illustrated in Figure 28, all the components in the experimental set-up are the same as the previous ones except the reactor cell. For this experiment, the reactor cell in Figure 27 has been connected in the circuit with nickel electrode plate as the anode and tungsten needle as the cathode.
Figure 28. Scheme of Experimental Set-up for Needle-to-liquid and Needle-to-solid Configurations

As illustrated in Figure 29, electrical discharges can be observed for both configurations. These discharges appear around the needle tip with a purple glow, which matches the feature of corona discharge. The V-I curves shown in Figure 30 also have high voltage at kilovolt level and symbolic voltage drop, and there is hardly any difference between these two curves.
Figure 29. Phenomena of Corona Discharge in Needle-to-liquid (A) and Needle-to-solid Configurations (B) in the Air

Figure 30. V-I Curves of Discharge in Needle-to-liquid and Needle-to-solid Configurations in the Air
Although the experimental results indicate no difference between these two configurations, the needle-to-plate configuration is considered as the easier way for CO\textsubscript{2} reduction process in the perspective of industrial operation.

In conclusion, through-gas discharge is more suitable for CO\textsubscript{2} reduction process because: (1) it is tough to generate electrical discharge in the liquids with high solubility of CO\textsubscript{2}, such as ionic liquid; (2) it is possible to generate multiple simultaneous discharges in gas phase. Therefore, the design and manufacture of the microscale-based corona reactor will be based on through-gas discharge needle-to-plate configuration.

3.2 Experimental Set-up and Reactor Geometry

Based on the conclusions from the previous experiments, an experimental set-up with multi-point corona reactor cell has been built, as illustrated in Figure 31. The operation will be through-gas, and the configuration of the reactor is needle-to-solid.

![Figure 31. Scheme of Experimental Set-up with Multi-point Corona Reactor Cell in Needle-to-solid Configuration](image-url)
There are eight components in the experimental set-up: CO₂ gas tank, mass flow controller, CO₂-water mixer, reactor cell, power supply, ballast resistor, measuring resistor and oscilloscope. The gas tank used in this experiment can provide ultra-high purity of CO₂ (99.9995% v/v), and the flow rate of CO₂ stream out of the cylinder can be controlled by the mass flow controller (Brooks 5850i series, calibrated for CO₂, 0–200sccm). The CO₂-water mixer is a glass bottle filled with glass beads and water. The inlet streamline of the mixer is submerged in the water with a slip-on inlet filter installed (for 1/8”i.d. tubing) so that the smaller bubble size can be obtained and CO₂ and water can be well mixed, and the outlet streamline is above the liquid level. The gas chromatograph used in this study is an SRI 8610C with helium ionization detector (HID), and two columns are installed in series: Haysep-D and Molecular Sieve 13x. The power supply used in this experiment is a high-voltage DC power supply (Glassman EQ series, current: 0~120mA; voltage: 0~10kV), and ballast resistor with a resistance of 1MΩ and measuring resistor with a resistance of 1MΩ were used. The role of ballast resistor is to protect power supply and other components in the circuit. The oscilloscope was used to measure the voltages across reactor cell and measuring resistor respectively. Channel 1 is for reactor cell, and Channel 2 is for measuring resistor. The current in the circuit can be calculated with the voltage and resistance of measuring resistor, and plot of voltage across reactor cell versus current can be produced.

The core of the experimental set-up is the reactor cell, as shown in Figure 32 and Figure 33. It has six components: polycarbonate top plate, neoprene O-ring, nickel electrode plate, screw for electrical connection, tungsten needles and polycarbonate bottom plate. On the top plate, two through holes in the middle of the top face are manufactured for inlet and outlet stream and eight screw holes around for assembly. A deep narrow groove on the top surface of the bottom plate is used as the reaction channel, and a shallow square ring notch on the same surface is prepared for O-ring. Three narrow through holes on one of the longitude side are drilled for three tungsten needles while one through hole with threads on the opposite side is machined for the electrical connection screw. The nickel electrode plate is attached on the side of narrow deep notch closer to the screw and together serves as the anode. The three tungsten needles were prepared the electrolysis
etching method mentioned above and are used as the cathode. The gaps between needles and nickel plate are the places where electrical discharge supposed to occur and the gap distances can be adjusted by moving the needles.

Figure 32. Photograph of Reactor Cell with Three Corona Points in Needle-to-solid Configuration

Figure 33. Scheme of Reactor Cell with Three Corona Points in Needle-to-solid Configuration (Smaller Active Volume Ratio)
The active volume ratio is considered as one of the factors that can influence the performance of the reactor cell. The scheme of the structure of the reaction channel for the reactor cell with three corona points is plotted in Figure 34 and the calculation of the active volume ratio is shown below:

\[ V_{\text{whole}} = L \cdot W \cdot H - 3 \times \left( \pi r^2 h_1 + \frac{1}{3} \pi r^2 h_2 \right) \]

\[ = 47\text{mm} \times 2.54\text{mm} \times 10.2\text{mm} - 3 \times \pi \left( \frac{1.5875\text{mm}}{2} \right)^2 \times \left( 1.04\text{mm} + \frac{1}{3} \times 1\text{mm} \right) \]

\[ = 1185\text{mm}^3 = 1.185\text{cm}^3 \]  

(Eq. 3-5)

\[ V_{\text{active}} = 3 \times \pi r^2 d = \pi \left( \frac{1.5875\text{mm}}{2} \right)^2 \times 0.5\text{mm} = 11.85\text{mm}^3 = 0.01187\text{cm}^3 \]  

(Eq. 3-6)

\[ \phi = \frac{V_{\text{active}}}{V_{\text{whole}}} = \frac{0.01187\text{cm}^3}{1.185\text{cm}^3} = 1.00\% \]  

(Eq. 3-7)

Figure 34. Scheme of the Structure of Reaction Channel in the Three-Corona Points Reactor Cell
Another reactor cell with larger active volume ratio was built, as illustrated in Figure 35. This reactor cell has five components: six copper needles, polycarbonate top plate, nickel electrode plate, polycarbonate bottom plate and copper electrical connection wire. The top plate and bottom plate can be assembly through four screw holes on the four corners, and they can be sealed by a joint formed by a notch on the top surface of the bottom plate and a fitted projection on the bottom surface of the top plate. On the top plate, there are six narrow through holes on the top surface for six copper needles. These six copper needles are used as the cathode. On the bottom plate, there is a deep narrow notch beneath the previous one used as the reaction channel with two connection holes in the front and back as the inlet and outlet and one through hole for the copper electrical connection wire. The nickel electrode plate is positioned on the bottom the second notch, and copper electrical connection wire contacts this plate from the back side, together as the anode.

Figure 35. Scheme of Reactor Cell with Six Corona Points in Needle-to-solid Configuration (Larger Active Volume Ratio)
The copper needles on the top plate were prepared using the chemical etching method. The procedure of the chemical etching is illustrated in Figure 36 and is listed below:

(1) Cut and straight six copper wires and plug them into the six holes on the top plate, making sure the length of exposed part on the side with projection is only a little more than the desired needle height, and then fixed the needles on the other side using epoxy;

(2) Cut a piece of rubber into the same size as the projection part on the top plate with a rectangular through hole in the middle and cover it on the projection so that the square hole becomes a reservoir;

(3) Fill tetrachloroethylene (CCl$_2$=CCl$_2$) first until the depth of the organic layer reaches the desired needle height, and then fill nitric acid (HNO$_3$). During the process, bubbles were generated at the interface of the organic layer and nitric acid layer, while the copper wires were etched around the interface into a biconcave shape because of mass transfer and fluid dynamics. Eventually, when the wire around the interface is thin enough, the gravity will drop the upper part of copper wires, leaving the bottom part as the desired part. The electrochemical reactions occurred on cathode and anode are as follows:

Cathode: $NO_3^- + 2H^+ + e^- \rightarrow NO_2(g) + H_2O$ \hspace{1cm} (Eq. 3-8)

Anode: $Cu(s) \rightarrow Cu^{2+} + 2e^-$ \hspace{1cm} (Eq. 3-9)

Overall: $Cu(s) + 2NO_3^- + 4H^+ \rightarrow Cu^{2+} + 2NO_2(g) + 2H_2O$ \hspace{1cm} (Eq. 3-10)
The active volume ratio of the second reactor cell is calculated, as shown below in (Eq. 3-11) \sim (Eq. 3-13), and these two reactor cells are compared in the perspectives of phenomena, V-I curves, and conversions of CO₂. Due to some manufacturing issues, discharges can only be generated simultaneously on two out of six needles, but even in this case, the active volume ratio in this reactor cell is still much larger than the previous one.

\[ V_{\text{whole}} = L \cdot W \cdot H - 6 \times \left( \pi r^2 h_1 + \frac{1}{3} \pi r^2 h_2 \right) \]

\[ = 10.16\, mm \times 1.32\, mm \times 1.93\, mm - 6 \times \pi \times \left( \frac{1.27\, mm}{2} \right)^2 \times \left( 0.93\, mm + \frac{1}{3} \times 0.5\, mm \right) \]

\[ = 17.55\, mm^3 \]  
(Eq. 3-11)

\[ V_{\text{active}} = 2 \times \pi r^2 d = 2 \times \pi \times \left( \frac{1.27\, mm}{2} \right)^2 \times 0.5\, mm = 1.27\, mm^3 \]  
(Eq. 3-12)

\[ \phi = \frac{V_{\text{active}}}{V_{\text{whole}}} = \frac{1.27\, mm^3}{17.55\, mm^3} = 7.24\% \]  
(Eq. 3-13)
3.3 Experimental Results

3.3.1 Discharge Phenomena

As illustrated in Figure 37, in the reactor cell with three corona points, corona discharges can be generated simultaneously in all three needle-plate gaps with the presence of either air or CO2. The discharges in the air appear around the needle tips with purple glows (see Figure 37 A) while the ones in CO2 release bluish-white glows (see Figure 37 B). A similar phenomenon also appears in the reactor cell with six corona points (see Figure 38). Although corona discharges can be generated simultaneously in only two needle-plate gaps due to some machining issues, the color of the discharges in CO2 is also bluish-white.

Figure 37. Phenomena of Discharges in the Air (A) and CO2 (B) in the Reactor Cell with Three Corona Points (Smaller Active Volume Ratio)
Figure 38. Phenomena of Discharges in CO$_2$ in the Reactor Cell with Six Corona Points (Larger Active Volume Ratio)

3.3.2 V-I Curves

The V-I curves in these two reactor cells are compared in Figure 39. These two curves were measured with the presence of CO$_2$, and both have high voltage at kilovolt level and symbolic voltage drop, and there is hardly any difference between these two curves.

Figure 39. V-I Curves of Discharges in CO$_2$ in the Reactor Cell with Three Corona Points (Smaller Active Volume Ratio) and Six Corona Points (Larger Active Volume Ratio)
3.3.3 Conversions

The gas chromatography results of CO$_2$ reduction in two reactor cells are respectively illustrated below in Figure 40 and Figure 41. Two kinds of reactants were tested: dry CO$_2$ and wet CO$_2$ (molar ratio of CO$_2$ and water $\approx$ 3:2). The products for the reduction of dry CO$_2$ is carbon monoxide (CO) and oxygen (O$_2$) while there is one more product for the reduction of wet CO$_2$: methane (CH$_4$). The same result occurs in both reactor cells, but the conversions of CO$_2$ are different in two reactor cells. In the reactor cell with smaller active volume ratio, the conversion of dry CO$_2$ and wet CO$_2$ are respectively 0.48% and 0.54%, while in the reactor cell with larger active volume ratio, the conversion of dry CO$_2$ and wet CO$_2$ are respectively 3.75% and 3.98%.

![Gas Chromatography Results for CO$_2$ Reduction in the Reactor Cell with Three Corona Points (Smaller Active Volume Ratio) with Trace of Impurity Nitrogen](image-url)
Figure 41. Gas Chromatography Results for CO₂ Reduction in the Reactor Cell with Six Corona Points (Larger Active Volume Ratio)

Figure 42 illustrates the comparison results of two reactor cell regarding the conversion of CO₂. It can be concluded that larger active volume ratio can lead to a higher conversion of CO₂ in the whole reactor channel while the conversion of CO₂ in the active volume remains the same for different active volume ratio.
3.4 Summary of Proof-of-concept Experiments

Through-gas reactor configuration and needle-to-plate design were determined as the suitable reactor design for the reduction of CO$_2$. Two through-flow microscale-based corona reactors with different active volume ratios were designed and manufactured. Reduction of CO$_2$ can be achieved in these two reactors at room temperature. The conversions of CO$_2$ in these two reactors were compared, and larger active volume ratio results in higher conversion.

References


51. Maezono, I.; Chang, J.-S., Reduction of CO$_2$ from Combustion Gases by DC Corona


68. Miao, Y. CO\textsubscript{2} Reduction in Aqueous-Ionic Liquid Solution in Microscale-Based Corona Reactor. Oregon State University, Corvallis, OR, 2013.


Chapter 4- CO2 Reduction in Mutli-discharge Microscale-based Reactor

Global warming caused by the emission of greenhouse gasses has created extremely negative environmental impacts, such as the rise of sea level, the disappearance of lakes and rivers, and melting of the ice caps. Among various greenhouse gasses, carbon dioxide (CO2) is considered as the most important one, because of its greenhouse properties and continuous accumulation in the atmosphere.1, 2 Indeed, carbon dioxide accounts for about 82% of all U.S. greenhouse gas emissions in 2013 from human activities such as generation of electricity, transportation, and various industrial activities.5 Consequently, the need to control CO2 production and emissions is the center of attention of both scientific and industrial worlds, and several methods have been developed to achieve this goal.2

Any success in the research and development of a feasible CO2 utilization method would signify the achievement of two objectives: (1) to slow down the accumulation of greenhouse gasses in the atmosphere; and (2) to provide better carbon resource utilization. However, due to the low energy content of CO2, a significant amount of additional energy (would, in turn, induce more CO2 emission) is required for the conventional catalytic reduction of CO2.48

Recently, non-thermal plasma has attracted much attention with regards to the effective and efficient industrial applications. The electrons in non-thermal plasma can reach temperatures of 10^4~10^5K (1~10eV) while the gas temperature can remain as low as room temperature. The high electron temperature determines the unusual chemistry of non-thermal plasmas. Non-thermal plasma can exist as several different types, including glow discharge, corona discharge, dielectric barrier discharge (DBD), microwave discharge, and radio frequency (RF) discharge, based on mechanisms of plasma generation, applied pressure, and electrode geometry.49, 50 Among these types of non-thermal plasmas, corona discharge is considered as the efficient technique. Corona discharge is a low-energy electrical discharge with non-thermal ionization that takes place in the vicinity of an electrode of a sufficiently low radius of curvature, in an atmospheric pressure medium.71, 72 It is self-sustained and no external energy other than
the electrical is needed to sustain the gas ionization and to maintain the current flow. Besides, it can only operate at a non-uniform electrode geometry. One of the most practical electrode configurations is multipoint to plane geometry, which is more suitable for industrial applications. In this configuration, the space charge produced by the adjacent points effects on the discharge current from the other points.\textsuperscript{72}

The significance of microtechnology has dramatically increased over the last few years in electrical applications. A microelectromechanical system (MEMS) holds the advantages of portability, scalability by numbering up, reduced waste, and improved mass and energy transfer characteristics.\textsuperscript{38} For the applications involving plasmas, microscale is the only reactor size making it possible to access certain desirable plasma states at atmospheric pressure. Microtechnology improves upon conventional plasma reactors by enabling the plasma to operate at much lower power inputs and atmospheric pressure.\textsuperscript{73} These improved characteristics make microtechnology a suitable choice for chemical reactions in a plasma environment.

In the previous study, experiments were conducted to determine the most appropriate configuration of the reactor: through-gas needle-to-plane system, and to decide the products for the reduction of dry and wet CO\textsubscript{2}. Based on this result, two multipoint microscale-based corona reactors were designed and built to investigate the effect of several factors on the performance of the reactor and energy efficiency, including active volume ratio, the flow rate of CO\textsubscript{2}, operation point in different regime on V-I curve, CO\textsubscript{2}-to-H\textsubscript{2}O molar ratio and the distribution of corona points.
4.1 Experimental Set-up and Multi-discharge Reactor Geometry

4.1.1 Experimental Set-up

The schemes for the experimental set-up test loop are illustrated in Figure 43 and Figure 44. In Figure 43, the solid line, red dash-dot line and green dotted line respectively represent the material pathway, electrical pathway and oscilloscope connections.

![Figure 43. Schematic Representation of CO₂ Reduction Test Loop](image)

Before entering the corona reactor, the CO₂ flow (ultra-high purity, 99.9995% v/v) mixes with liquid water from a syringe pump (Harvard Apparatus PHD 2000 series) in the evaporator and the fluid is heated to and remains around 110°C to become a mixture of CO₂ and water vapor. A mass flow controller (Brooks 5850i series, calibrated for CO₂, 0~200sccm) is used to control the flow rate of CO₂. This high-temperature mixture flows into the reactor as the reactant stream. A temperature control box keeps the temperature in the reaction channel constant at 110°C to prevent the water vapor from condensation.
The effluent stream flows to the gas chromatograph (SRI 8610C series, helium ionization detector, columns: Hayesep-D and Molecular Sieve 13x), and the concentrations of reactants and products are determined according to the chromatography.

Electrical energy provided by a high-voltage DC power supply (Glassman ET series, current: 0~660mA; voltage: 0~3kV) drives the reaction. A 1MΩ ballast resistor positioned closer to the positive side of the power supply is in series with the reactor and is used to regulate the applied power. A 1MΩ measuring resistor located closer to the negative side of the power supply is also connected in series and is used for the convenience of calculation of the current. Voltages across the reactor and the measuring resistor are monitored through an oscilloscope (Tektronix TDS 700D series, channel 1 for the reactor, channel 2 for measuring resistor). The current through the circuit can be calculated using the following equation:

\[
I = \frac{\text{Voltage across the measuring resistor}}{\text{Resistance of the measuring resistor}}
\]

(Eq. 4-1)

**Figure 44. Photo of CO₂ Reduction Test Loop**
4.1.2 Multi-discharge Reactor Geometry

1. Corona Microreactor with 200-pin Plate

As illustrated in Figure 45 and Figure 46, a multi-point microscale-based corona reactor with a 200-pin plate was manufactured. Along with some assembly parts (screws, bolts, washers and O-ring), this reactor cell contains six primary components: stainless steel top plate, needle plate, PEEK bottom plate, distributors, spacers, and screw back.

Figure 45. Scheme of Multi-point Micro-scaled Corona Reactor with 200-pin Plate
The needle plate (see Figure 47) is the core of this reactor cell. It is made of cobalt chrome, which is chosen for its high-temperature resistance. This plate is manufactured using direct metal laser sintering (DMLS), a metal 3D-printing method that can build complex geometries layer-by-layer (down to 20 microns) directly from 3D CAD data. As illustrated in Figure 48, the needles on the plate are in a cone shape with round base in diameter of 550µm and height of 600µm, and they are orderly arranged. The arrangement of needles on the plate is 20 × 10 arrays with a peak-to-peak distance of 800µm in longitude direction and 500µm in latitude direction. On the back side of this 200-pin plate, there are four posts with the threaded blind hole on each post. Four threaded copper bars are attached and used as electrical connections. The needle plate and four copper bars together serve as the cathode electrode.
As illustrated in Figure 45, the top plate is made of stainless steel, and there are inlet and outlet channels inside the plate and there is an electrical connection port outside. This top plate is served as the anode electrode. The bottom surface of this plate is precision grounded, and the variances of the flatness and parallelism are 0.000mm (accuracy of 0.001mm). A round silicone heat sheet was attached to the top surface of this plate to keep the temperature constant at 110°C.

As shown in Figure 45, the bottom plate is made of PEEK. It has a notch in the middle of the top surface to install the needle plate, two PEEK distributors, and two PEEK spacers. The distributors are used for uniformly distributing the inlet and outlet streams and forming a pressure drop section over the reaction area. The spacers are primarily used to fixate the needle plate. There are four through holes in this notch so that the four posts on the back side of needle plate can pass through. There is another shallow round groove for the O-ring around the previous one. Four through holes with threads in the four corners are for the assembly purpose. The screw back part is also made of PEEK, and it is a rectangular slotted container. The inner depth is same as the height of the posts on the back of the needle plate. There are four through holes at the bottom, and the size of these holes fits the copper bars used for electrical connections. The primary purpose of the screw back is for fixating the needle plate.
2. Corona Microreactor with 100-pin Plate

A reactor cell as shown in Figure 49 and Figure 50 was manufactured. Along with some assembly parts (screws, bolts, and washers), this reactor cell contains seven primary components: cartridge heater holder plate, stainless steel top plate, Teflon middle plate, stainless steel needle plate, Teflon bushings, stainless steel electrode plate and Teflon bottom plate.

![Diagram of Corona Microreactor components]

Figure 49. Scheme of Multi-point Micro-scaled Corona Reactor

![Photo of Corona Microreactor]

Figure 50. Photo of Multi-point Micro-scaled Corona Reactor
The needle plate is the core of this reactor cell (see Figure 51). It is made of stainless steel, which is chosen because of its relatively high-temperature resistance. This plate was manufactured using electrical discharge machining (EDM), a precise metal machining method using electrical discharges. As illustrated in Figure 52, the needles on the plate are square pyramids with a base of 200µm × 200µm and height of 500µm, and they are 90° to each other. The arrangement of needles on the plate is 10 × 10 arrays with a peak-to-peak distance of 500µm.

![Figure 51. Photo of Stainless Steel Needle Plate with 100 pins in the Package](image1)

Figure 51. Photo of Stainless Steel Needle Plate with 100 pins in the Package

![Figure 52. SEM Micrograph of Stainless Steel Needle Plate](image2)

Figure 52. SEM Micrograph of Stainless Steel Needle Plate

Figure 53 illustrates the Teflon middle plate with the needle plate installed. The middle plate has a notch in the center of the top surface, and it is used as the reaction channel. Two porous PTFE distributors (pore size = 40–60µm) are installed in the notch and are used for uniformly distributing the inlet and outlet streams and forming a pressure drop.
section over the reaction area. A square hole was cut from the bottom, and the edges of this square hole are at an angle of 45° with the edges of the plate. The majority of this square hole was cut through, leaving two corners blind-cut used for holding the needle plate. The needle plate is installed in the middle plate in the way as shown in Figure 53. The variance between the thicknesses of the square hole and needle plate was checked using ZeScope optical profiler, and found to be less than 0.5µm.

Figure 53. Photo of Teflon Middle Plate with Needle Plate Installed Before the Decrease of Bypass Volume

To improve the active volume ratio, four triangular Teflon spacers (3.56mm × 1.40mm × 0.237mm) were used to cover the four corners and RTV silicone coating was applied to fill some bypass volume between needles, as shown in Figure 54. The thickness of the RTV silicone coating is 373µm, measured by ZeScope optical profiler.

Figure 54. Photo of Teflon Middle Plate with Needle Plate Installed After the Decrease of Bypass Volume
The top plate shown in Figure 49 is made of stainless steel. There are two through holes used as the inlet and outlet channels and one threaded blind hole used as the electrical connection port. The top and bottom surfaces of this plate are precision grounded, and the variances of the flatness and parallelism are 0.000mm (accuracy of 0.001mm). A narrow notch across the plate is used for holding the cartridge heater. The cartridge heater holder plate assembled on top is stainless steel, and can fixate the heater. These two plates together are used as the anode electrode.

The stainless steel electrode plate shown in Figure 49 is placed beneath the middle plate, and it contacts the needle plate. This electrode plate is used as cathode electrode together with needle plate. This plate is longer than the other plates, and a threaded blind hole on the extra part is used as the electrical connection port. The top and bottom surfaces of this electrode plate are also precision grounded, and the variances of the flatness and parallelism are 0.000mm (accuracy of 0.001mm). The screw holes on this plate are larger than those on the other plates, and four Teflon bushings placed in these four screw holes are used as electrical insulation between screws and electrode plate so that anode and cathode are not connected. The Teflon bottom plate placed under this electrode plate is used as the protection.

4.2 Experimental Results

4.2.1 Discharge Phenomena

In order to visualize the corona discharge, a fluorine-doped tin oxide (FTO) glass substrate was used as the counter electrode because of its electrical conductivity, high-temperature resistance, and translucence. Besides, corona discharge can leave a trail on the counter electrode surface, which is another evidence to prove the appearance of corona discharge.

As illustrated in Figure 55 A, corona discharges were only observed on parts of the needles on the 200-pin plate, and all of these needles are focused on one side of the plate along the longitude direction. The flow direction is also along the longitude direction, which leads to the reduction of the reactor efficiency. The trails of corona discharges on
FTO glass substrate and stainless steel plate, as illustrated in Figure 55 B and C, also indicate that corona discharges were only generated on parts of the needles.

**Figure 55.** (A) Phenomena Through the FTO Glass Substrate on the Corona Reactor with 200-pin Plate; (B) Trail of Corona Discharges on FTO Glass Substrate; (C) Trail of Corona Discharges on Stainless Steel Top Plate

This problem was further investigated, and the distances between the bottom surface of the needle plate and the tip of the needles ($d$ in the left picture of Figure 56) at eight locations along the two longitude sides of the plate were measured on a microscope. The measurement result is illustrated in the right image of Figure 56, and the higher value of $d$ means the smaller gap distance between needle tip and the counter electrode which makes it easier to generate the corona discharge. Therefore, the phenomena in Figure 55 are due to the warping problem along the side where corona discharges were observed.
Figure 56. Illustration of Warping Problem on the 200-pin Plate

The most efficient solution to this warping problem is to divide the needle plate into halves and connect one of the half pieces into the circuit. The needle plate was cut into halves using electrical discharge machining (EDM). Before the experiment, both of the half pieces were still installed in the reaction channel of the bottom plate, but a piece of Teflon sheet was placed between them as electrical insulation. Figure 57 illustrates the phenomenon through FTO glass substrate and trail of corona discharge on FTO glass substrate when only half of the 200-pin needle plate was connected to the circuit. It can be observed that corona discharges were generated on most of the needles on the half plate.
For the corona reactor with a 100-pin plate, the phenomena and trails of corona discharge are illustrated in Figure 58. It can be observed from the pictures that most of the corona points can be generated simultaneously, and the corona discharges are uniform in shape. The diameters of corona discharge footprints were measured using a microscope, and the result is around 400µm. This dimension is useful for the calculation of the active volume ratio.
Figure 58. Discharges Observed through FTO Glass Substrate on the Corona Reactor with 100-pin Plate Before (A) and After (B) the Decrease of Bypass Volume; Trail of Corona Discharge on FTO Glass Substrate (C) and Stainless Steel Top Plate (D); Microscopic Graph of Footprint of Corona Discharge on Stainless Steel Top Plate (E)

4.2.2 V-I Curves

The V-I curves in these two corona reactors are compared in Figure 59. These two curves were measured with the presence of CO₂, and both have high voltage at kilovolt level and symbolic voltage drop. There is hardly any difference between the shapes of these two curves.
To further understand the behavior of the discharges, the oscillography of discharges in different regimes on V-I curve were compared, as shown in Figure 60. The minimum time step of sampling is 40 nanosecond. It can be observed that discharge in spark regime is pulsing in a regular pattern, and the pulses occur when the intense electrons generated by electron avalanche are attached to the cathode in a short time. By contrast, the discharge in glow regime is more continuous and stable because the entire gap is full of negative ions and the ionization is created through the gap. The oscillography of discharge in arc regime illustrates an irregular pattern because the energy of electrons is used to accelerate the movement of larger particles, which also explains the high thermal intensity of arc discharge.
Figure 60. Comparison of Oscillography of Discharges in Different Regimes of V-I Curve (Top: Voltage across Corona Reactor; Bottom: Voltage across Measuring Resistor, Corresponding to the Current)
The relationships among the voltages across the reactor and voltage across measuring resistor at different regimes are respectively illustrated in Figure 61 and Figure 62.

**Figure 61. Relationships among the Voltages across the Reactor at Different Regimes** (Top: $V_{\text{spark}} > V_{\text{glow}}$, Bottom: $V_{\text{arc}} > V_{\text{glow}}$)
Figure 62. Relationships among the Voltages across the Measuring Resistor (Corresponding to the Current) at Different Regimes (Top: $I_{\text{glow}} > I_{\text{spark}}$; Bottom: $I_{\text{arc}} > I_{\text{glow}}$)
4.2.3 Conversions

1. Corona Microreactor with 200-pin Plate

In the corona reactor with a 200-pin plate, the active volume ratio was calculated, and experiments were conducted to study the influence of flow rate of CO$_2$ and distribution of corona points on the performance of the reactor.

(1) Calculation of Active Volume Ratio

The active volume ratio of the corona microreactor with a 200-pin plate can be calculated based on the dimensions of the needle plate:

Volume of the whole channel:

\[
V_{\text{whole}} = L \cdot W \cdot H - N \cdot \frac{\pi r^2 h}{3}
\]

\[
= 19\,\text{mm} \times 12\,\text{mm} \times 0.727\,\text{mm} - 200 \times \frac{\pi \cdot (0.55\,\text{mm})^2 \times 0.6\,\text{mm}}{3} \approx 127.76\,\text{mm}^3
\]

Active volume:

\[
V_{\text{active}} = n_c \cdot \pi \left( \frac{D}{2} \right)^2 d = 90 \times \pi \left( \frac{0.4\,\text{mm}}{2} \right)^2 \times 0.127\,\text{mm} \approx 1.44\,\text{mm}^3
\]

Active volume ratio:

\[
\phi = \frac{V_{\text{active}}}{V_{\text{whole}}} \approx 1.12\%
\]

Since the active volume ratio is only around 1%, the performance of the reactor is limited.

(2) Influence of Flow Rate of CO$_2$

**Figure 63** and **Figure 64** respectively illustrate the influence of different flow rate of CO$_2$ on the conversion of CO$_2$ in the whole reactor and the active volume. The three flow rates studied in this experiment are 20sccm, 30sccm, and 50sccm, respectively corresponding to mean residence time of 134ms, 89ms and 54ms while the time for electrons pass
through the gap is around $5.7 \times 10^{-5} \mu s$ (speed of electrons = 2200km/sec). All these data points were measured with constant CO$_2$-to-H$_2$O molar ratio (1:2) at the same operation point in glow regime (voltage = 0.870kV, current = 0.56mA).

![Figure 63](image1.png)

**Figure 63. Effect of Flow Rate of CO$_2$ on Conversion of CO$_2$ in the Whole Reactor (200-pin Plate)**

![Figure 64](image2.png)

**Figure 64. Effect of Flow Rate of CO$_2$ on Conversion of CO$_2$ in the Active Volume (200-pin Plate)**
It can be concluded that conversion of CO\(_2\) (both in the whole reactor and in active volume) increases with decreasing flow rate of CO\(_2\). Since the speed of reactants molecules is much smaller compared with the speed of electrons, the molecules can be treated as immobile while the electrons fly across the gap and collide with these molecules. The lower flow rate of reactants leads to a longer mean residence time of molecules and more chances of collisions.

(3) Influence of Distribution of Corona Points

**Figure 65** and **Figure 66** respectively illustrate the influence of the distribution of corona points on the conversion of CO\(_2\) in the whole reactor and the active volume. The first case is connecting a full plate to the circuit, and the distribution of corona points of this case is shown in **Figure 55A**. The second instance is connecting only half of the plate to the circuit while the other half is still installed in the channel but not electrical connected, and these two halves were separated by a piece of Teflon sheet. The distribution of corona points of the second case is illustrated in **Figure 57A**. It can be observed from **Figure 55A** and **Figure 57A** that the fluid flow passes through almost same amount of corona point in these two cases, but the distributions of corona points are different. All the data points were measured with a constant flow rate of CO\(_2\) (20sccm) and a consistent CO\(_2\)-to-H\(_2\)O molar ratio (1:2) at the same operation point in glow regime (voltage = 0.870kV, current = 0.56mA).
Figure 65. Effect of Distribution of Corona Points on Conversion of CO₂ in the Whole Reactor

It can be concluded that conversions of CO₂ (both in the whole reactor and in active volume) are higher when the flow direction is perpendicular to the distribution direction of corona points than parallel with the distribution direction. In the perpendicular case, the fluid flow passes through more corona points, and there are more opportunities to make the reactions occur.
2. Corona Microreactor with 100-pin Plate

On this corona reactor with a 100-pin plate, experiments were conducted to study the influence of active volume ratio and the effects of three factors on the performance of the reactor: operation points in different regimes, flow rate of CO$_2$, and CO$_2$-to-H$_2$O molar ratio.

(1) Influence of Active Volume Ratio

Although this corona reactor with 100-pin plate has a larger active volume ratio than the one with 200-pin plate, some improvements need to be made to further decrease the bypass volume by putting Teflon covers on four corners of the reaction channel and filling RTV silicone coating between the needles, as shown below in Figure 67.

![Figure 67](image.png)

**Figure 67. Increasing Active Volume Ratio of Corona Reactor with 100-pin Plate by Putting Teflon Covers on Four Corners of the Reaction Channel and Filling RTV Silicone Coating between the Needles**

For the corona microreactor with a 100-pin plate, the active volume ratio before and after the improvement can be calculated based on the dimensions of needle plate:

Volume of whole channel before the improvement:
Volume of whole channel after the improvement:

\[
V_{\text{whole, after}} = L \cdot W \cdot H_1 - N \cdot \frac{a_1^2 h_1}{3} - 4 \times \frac{a \cdot b \cdot H_1}{2}
\]

\[
= 7.12 \times 7.60 \times 0.237 - 100 \times \frac{1}{3} \times (0.2 \times 0.0508)^2 \times 0.127 \approx 10.45 \text{ mm}^3
\]

Active volume:

\[
V_{\text{active}} = n_c \cdot \pi \left( \frac{D}{2} \right)^2 d = (100 - 10) \times \pi \times \left( \frac{0.4 \times 0.11}{2} \right)^2 \times 0.11 \approx 1.24 \text{ mm}^3
\]

Active volume ratio before the improvement:

\[
\phi_{\text{before}} = \frac{V_{\text{active}}}{V_{\text{whole, before}}} = \frac{1.24 \text{ mm}^3}{32.34 \text{ mm}^3} \approx 3.83\%
\]

Active volume ratio after the improvement:

\[
\phi_{\text{after}} = \frac{V_{\text{active}}}{V_{\text{whole, after}}} = \frac{1.24 \text{ mm}^3}{10.45 \text{ mm}^3} \approx 11.90\%
\]

As illustrated in Figure 69, the conversion of CO\textsubscript{2} in the whole reactor and active volume, energy efficiency and reactor efficiency are compared among the following four cases: spark regime (red point in Figure 68) before the improvement, spark regime after the improvement, glow regime (first orange point from the bottom in Figure 68) before the improvement and glow regime after the improvement.
Figure 68. V-I Curves for Multi-point Corona Reactors with 100-pin Plates with the Presence of CO₂ (Red Circle: Spark Regime; Orange Square: Glow Regime; Green Triangular: Arc Regime)

Figure 69. Comparison of Conversion of CO₂, Energy Efficiency and Reactor Efficiency before and after the Improvement of Active Volume
In Figure 69, it can be observed that conversion of CO₂, energy efficiency and reactor efficiency are improved after the increase of active volume, and they increase in the same multiple of increasing active volume ratio. However, conversions of CO₂ in the active volume are almost the same before and after the growth of active volume for the two points in spark and glow regime. This result indicates the importance of increasing active volume ratio, which matches the previous conclusion.

(2) Influence of Operation Points in Different Regimes of V-I Curve

Figure 70 and Figure 71 respectively illustrate the influence of operation points in different regimes of V-I curve on the conversion of CO₂ in the whole reactor and the active volume. The three regimes studied in this experiment are respectively spark regime (red circle in Figure 68), glow regime (orange squares in Figure 68) and arc regime (green triangular in Figure 68). All these data points were measured with a constant flow rate of CO₂ (50sccm) and a consistent CO₂-to-H₂O molar ratio (1:2).

![Glow regime](image)

Figure 70. Effect of Operation Points in Different Regimes of V-I Curve on Conversion of CO₂ in the Whole Reactor (100-pin Plate)
Figure 71. Effect of Operation Points in Different Regimes of V-I Curve on Conversion of CO$_2$ in the Active Volume (100-pin Plate)

It can be observed that conversions of CO$_2$ (both in the whole reactor and in active volume) are higher in the glow regime than spark regime and arc regime and in the glow regime conversions of CO$_2$ (both in the whole reactor and in active volume) increase with the growth of current. In conclusion, more activated electrons are helpful for the breakdown of reactant molecules through collision, which is the reason why glow regime is better than spark regime on the conversion of CO$_2$. However, the resistance of the discharge increases during the transition from glow discharge to arc discharge since voltage grows faster than current. Therefore, the cross-section area of discharge decreases and multi-discharge collapses to a single arc discharge, which reduces the conversion.

(3) Influence of Flow Rate of CO$_2$

**Figure 72** and **Figure 73** respectively illustrate the influence of different flow rate of CO$_2$ on the conversion of CO$_2$ in the whole reactor and the active volume. The three flow rates studied in this experiment are 20sccm, 50sccm, and 80sccm, respectively corresponding to mean residence time of 31ms, 13ms and 8ms while the time for electrons pass through the gap is around $5.0 \times 10^{-5}$µs (speed of electrons = 2200km/sec). All these data points
were measured with a constant CO₂-to-H₂O molar ratio (1:2) at the same operation point in glow regime (voltage = 0.814kV, current = 0.42mA).

**Figure 72. Effect of Flow Rate of CO₂ on Conversion of CO₂ in the Whole Reactor (100-pin Plate)**

**Figure 73. Effect of Flow Rate of CO₂ on Conversion of CO₂ in the Active Volume (100-pin Plate)**

The results in the two pictures above match the conclusion from the reactor with a 200-pin plate that conversions of CO₂ (both in the whole reactor and in active volume) are
increasing with the decreasing of the flow rate of \( \text{CO}_2 \).

(4) Influence of \( \text{CO}_2 \)-to-\( \text{H}_2\text{O} \) Molar Ratio

Figure 74 and Figure 75 respectively illustrate the influence of different \( \text{CO}_2 \)-to-\( \text{H}_2\text{O} \) molar ratio on the conversion of \( \text{CO}_2 \) in the whole reactor and the active volume. The four \( \text{CO}_2 \)-to-\( \text{H}_2\text{O} \) molar ratios studied in this experiment are 1:2, 1:0.67, 1:0.5 and 1:0 (\( \text{CO}_2 \) only). These ratios were chosen based on the general reaction equation:

\[
3\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CO} + \text{CH}_4 + 3\text{O}_2
\]  
(Eq. 4-10)

The ratio of 1:0.67 matches the ratio of stoichiometric numbers. The water is rich when the ratio equals to 1:2, while the water is lean when the ratio equals to 1:0.5. All these data points were measured with a constant flow rate of \( \text{CO}_2 \) (50sccm) at the same operation point in glow regime (voltage = 0.814kV, current = 0.42mA).

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**Figure 74. Effect of \( \text{CO}_2 \)-to-\( \text{H}_2\text{O} \) Molar Ratio on Conversion of \( \text{CO}_2 \) in the Whole Reactor (100-pin Plate)**
It can be observed that conversions of CO₂ (both in the whole reactor and in active volume) are slightly increased with the decreasing of CO₂-to-H₂O molar ratio. In conclusion, the increase of water content favors the forward reaction, which leads to a high conversion of CO₂.

4.3 Energy Analysis

Please see section 2.4 for detailed energy analysis procedure.

4.3.1 Corona Microreactor with 200-pin Plate

The influences of two factors (flow rate of CO₂ and distribution of corona points) on the energy efficiency and reactor efficiency have been studied on this corona microreactor with a 200-pin plate.

1. Influence of Flow Rate of CO₂

Figure 76 and Figure 77 respectively illustrate the influence of different flow rate of CO₂ on energy efficiency (see Eq. 4-17) and reactor efficiency (see Eq. 4-18). The three flow rates studied in this experiment are 20sccm, 30sccm, and 50sccm, respectively
corresponding to mean residence time of 134ms, 89ms and 54ms while the time for electrons pass through the gap is around 58 sec. All these data points were measured with a constant CO$_2$-to-H$_2$O molar ratio (1:2) at the same operation point in glow regime (voltage = 0.870kV, current = 0.56mA).

Figure 76. Effect of Flow Rate of CO$_2$ on Energy Efficiency (200-pin Plate)

Figure 77. Effect of Flow Rate of CO$_2$ on Reactor Efficiency (200-pin Plate)
It can be observed that energy efficiency and reactor efficiency are increasing with the growth of flow rate of CO$_2$. As explained previously, the molecules is immobile compared with electrons due to much lower speed, which leads to a longer mean residence time of molecules. However, staying longer in the reaction zone increases the possibility of multiple collisions of molecules from electrons, which can lower the energy efficiency and reactor efficiency.

2. Influence of Distribution of Corona Points

Figure 78 and Figure 79 respectively illustrate the influence of the distribution of corona points on energy efficiency (see Eq. 4-17) and reactor efficiency (see Eq. 4-18). The first case is connecting a full plate to the circuit, and the distribution of corona points of this case is shown in Figure 55A. The second instance is connecting only half of the plate to the circuit while the other half is still installed in the channel but not electrical connected, and these two halves were separated by a piece of Teflon sheet. The distribution of corona points of the second case is illustrated in Figure 57A. It can be observed that the fluid flow passes through the same amount of corona point in these two cases, but the distributions of corona points are different. All the data points were measured with a constant flow rate of CO$_2$ (20sccm) and a consistent CO$_2$-to-H$_2$O molar ratio (1:2) at the same operation point in glow regime (voltage = 0.870kV, current = 0.56mA).

![Figure 78. Effect of Distribution of Corona Points on Energy Efficiency](image-url)
It can be concluded that energy efficiency and reactor efficiency are higher when the flow direction is perpendicular to the distribution direction of corona points than parallel with the distribution direction. In the perpendicular case, the fluid flow passes through more corona points, and there are more opportunities to use the energy for reactions.

4.3.3 Corona Microreactor with 100-pin Plate

The influences of three factors (operation points in different regimes, flow rate of CO₂, and CO₂-to-H₂O molar ratio) on the energy efficiency and reactor efficiency have been studied on this corona microreactor with 100-pin plate.

1. Influence of Different Points on V-I Curve

**Figure 80** and **Figure 81** respectively illustrate the influence of operation points in different regimes of V-I curve on energy efficiency (see Eq. 4-17) and reactor efficiency (see Eq. 4-18). The three regimes studied in this experiment are respectively spark regime (red circle in **Figure 68**), glow regime (orange squares in **Figure 68**) and arc regime (green triangular in **Figure 68**). All these data points were measured with a constant flow rate of CO₂ (50sccm) and a consistent CO₂-to-H₂O molar ratio (1:2).
Figure 80. Effect of Operation Points in Different Regimes of V-I Curve on Energy Efficiency

Figure 81. Effect of Operation Points in Different Regimes of V-I Curve on Reactor Efficiency

It can be observed that energy efficiency and reactor efficiency are much lower in the arc
regime than glow regime and spark regime because arc discharge is thermal intense and most of the energy are lost in heat because of the vibration of molecules. Besides, in the glow regime energy efficiency and reactor efficiency are independent to the current.

2. Influence of Different Flow Rate of CO$_2$

**Figure 82** and **Figure 83** respectively illustrate the influence of different flow rate of CO$_2$ on energy efficiency (see Eq. 4-17) and reactor efficiency (see Eq. 4-18). The three flow rates studied in this experiment are 20sccm, 50sccm, and 80sccm, respectively corresponding to mean residence time of 31ms, 13ms and 8ms while the time for electrons pass through the gap is around 50 sec. All these data points were measured with a constant CO$_2$-to-H$_2$O molar ratio (1:2) at the same operation point in glow regime (voltage = 0.814kV, current = 0.42mA).

![Figure 82. Effect of Flow Rate of CO$_2$ on Energy Efficiency (100-pin Plate)](image-url)
The results in the two pictures above match the conclusion from the reactor with a 200-pin plate that energy efficiency and reactor efficiency are increasing with the growth of flow rate of CO₂.

3. Influence of Different CO₂-to-H₂O Molar Ratio

Figure 84 and Figure 85 respectively illustrate the influence of different CO₂-to-H₂O molar ratio on energy efficiency (see Eq. 4-17) and reactor efficiency (see Eq. 4-18). The four CO₂-to-H₂O molar ratios studied in this experiment are 1:2, 1:0.67, 1:0.5 and 1:0 (CO₂ only). These ratios were chosen based on the general reaction equation (see Eq. 4-7). The ratio of 1:0.67 matches the ratio of stoichiometric numbers. When the ratio equals to 1:2, the water is rich, while the water is lean when the ratio equals to 1:0.5. All these data points were measured with a constant flow rate of CO₂ (50sccm) at the same operation point in glow regime (voltage = 0.814kV, current = 0.42mA).
Figure 84. Effect of CO$_2$-to-H$_2$O Molar Ratio on Energy Efficiency

![Energy Efficiency Chart]

Figure 85. Effect of CO$_2$-to-H$_2$O Molar Ratio on Reactor Efficiency

![Reactor Efficiency Chart]

It can be observed that energy efficiency and reactor efficiency can reach maximum when CO$_2$-to-H$_2$O molar ratio matches the ratio of stoichiometric numbers. It matches the expectation that the excess reactants (CO$_2$ or H$_2$O) cannot completely react and can cause energy loss.
4.4 Summary of Experiments in Multi-discharge Reactor

1. The corona microreactor with 200-pin plate:

(1) Conversion of CO\textsubscript{2} is increasing with the decreasing flow rate of CO\textsubscript{2}, but higher energy efficiency and reactor efficiency can be achieved at a higher flow rate of CO\textsubscript{2}. The optimal flow rate of CO\textsubscript{2} depends on the location of this CO\textsubscript{2} reduction system installed in the industrial pipeline. If it is installed at the beginning for the generation of CH\textsubscript{4} and CO, a higher flow rate is preferred because the separation of products is an energy-consuming process and higher energy efficiency of the CO\textsubscript{2} reduction system is preferred. However, if this system is installed at the end of the pipeline to prevent CO\textsubscript{2} from releasing to the atmosphere, a lower flow rate is preferred because the conversion of CO\textsubscript{2} is more important.

(2) Since the corona points were not generated on all of the pins in this reactor, the distribution direction of corona points can play a role in the performance. Performance of the reactor and energy efficiency are higher when the flow direction is perpendicular to the distribution direction of corona points than parallel with the distribution direction. In the perpendicular case, the fluid flow passes through more active corona points, and there are more opportunities to make the reactions occur, but in the parallel case, part of the flow does not pass through any active corona point.

2. The corona microreactor with 100-pin plate:

(1) The conversion of CO\textsubscript{2} is higher in glow regime than spark regime and arc regime, and it reaches the maximum in the glow regime with the highest current. The energy efficiency and reactor efficiency are higher in this regime than spark regime and arc regime, and these efficiencies are nearly the same in the glow regime. Therefore, the optimal operation point is the one in the glow regime with the highest current (voltage = 0.840kV, current = 0.62mA).

(2) The same conclusion can be made about the influence of flow rate of CO\textsubscript{2} on the performance of this microreactor with 100-pin plate that conversion of CO\textsubscript{2} is
increasing with the decreasing flow rate of CO₂, but higher energy efficiency and reactor efficiency can be achieved at a higher flow rate of CO₂.

(3) The conversion of CO₂ is slightly higher when the water content is greater. The energy efficiency and reactor efficiency are higher when CO₂-to-H₂O molar ratio matches the ratio of stoichiometric numbers. Therefore, the optimal CO₂-to-H₂O molar ratio is at somewhere between 1:2 and 1:0.67 for the balance of high conversion and high energy efficiency.

3. The corona microreactor with a 100-pin plate is better than the one with a 200-pin plate at the perspectives of chemical conversion and energy consumption. This result is due to the higher quality of manufacturing on the 100-pin reactor which has more corona points generated on the pins and a smaller gap between pins. These can be helpful for improving the active volume ratio.

References


Chapter 5- CO₂ Reduction Finite Element Modeling of Reaction Data from Multi-discharge Microreactor

CO₂ is considered as one of the primary cause of global warming, and among various methods of CO₂ utilization, conversion of CO₂ to value-added chemical products is the most attractive. The introduction of both microtechnology and application of non-thermal plasma for CO₂ reduction is very promising because of the high efficiency in chemical conversion and energy consumption.

Mathematical model and numerical simulations of chemical reaction process in plasma can be useful in many perspectives. An improved understanding of the reaction system can be achieved by comparing predictions from numerical simulations with experimental observations. Modeling and simulations based on reliable physical and chemical modeling of a plasma-involved system can significantly reduce the number of associated experiments that otherwise would have to be performed.

Among the various numerical simulation tools, COMSOL Multiphysics is a finite element analysis software program that provides the means to model engineering designs and simulate potential failure modes. The program allows exploration of various assumptions, design geometries, and boundary conditions, and enables users to visually and quantitatively analyze the implications of different design decisions. Its simulation environment facilitates all the steps in the modeling process – defining geometry, meshing, specifying physics, solving, and then visualizing results. It also serves as a platform for the application specific modules. A number of predefined physics interfaces lead to a quick model set-up. Also, the COMSOL Multiphysics user interface gives the option to specify partial or ordinary differential equations (PDEs or ODEs) and link them with other physics interfaces.⁷⁴

In this study, a mathematical model is developed describing the performance of the multi-discharge microscale-based corona reactor for CO₂ reduction process. The mathematical model includes conservation laws (momentum balance and material balance) and kinetics. COMSOL Multiphysics is used to build a numerical model simulating this
process, and its extensive interface COMSOL-Matlab LiveLink is used to extract the kinetic parameters in this process. The determined kinetic parameters are then used to predict the experimental output of the reactor, and the predictive robustness of the numerical model is evaluated by comparing with previous experimental results.

5.1 Geometry and Mesh

The particular geometry to be modeled mimics the reaction channel of corona reactor with 100-pin plate. Because the complexity of the geometry on the x-z planar, a 3D model is required to investigate the velocity profile and concentration profile in the reaction channel. As illustrated below in Figure 86, the geometry is composed of a hexagonal prism part with 100 cylinder holes and another part with 100 cylinders as the activated discharge regions, and these two parts were drew using SolidWorks and imported into COMSOL Multiphysics. In this geometry, the y coordinate is specified as a thickness of 110μm, which represents the gap distance between needle tips and the counter electrode plate. The fluid flow direction is along the z coordinate, and the highlighted surfaces in the picture respectively represent the inlet and outlet.

![Figure 86. Geometry of Modeling Subject](image-url)
A fine mesh has been applied to the microreactor geometry to make sure the simulation result is as accurate as possible under the premise of less computationally expensive. The maximum and minimum element sizes of the mesh are respectively $5.1 \times 10^{-5} \text{m}$ and $9.63 \times 10^{-6} \text{m}$, and the maximum element growth rate is 1.13. A finer mesh has been applied at the boundaries of activated discharge region to make sure the continuity of concentration profile. The maximum and minimum element size of the mesh is respectively $3.65 \times 10^{-5} \text{m}$ and $3.85 \times 10^{-6} \text{m}$, and the maximum element growth rate is 1.1.

5.2 Conservation Laws

5.2.1 Momentum Balance

1. Assumptions:

(1) The fluid is Newtonian;

(2) The flow is laminar (see Appendix E for calculation of Reynolds number) and isothermal;

(3) Compressible flow, but the Mach number $M < 0.3$, so the change in the density and temperature of the fluid can be neglected

(4) Steady state condition, $\frac{\partial v_x}{\partial t} = \frac{\partial v_y}{\partial t} = \frac{\partial v_z}{\partial t} = 0$

(5) No velocity in $x$ and $y$ direction, $v_x = 0, v_y = 0$

(6) No velocity change along the $x$ direction, $\frac{\partial v_x}{\partial x} = 0$

(7) Neglect gravity, $g_x = g_y = g_z = 0$

(8) The distance along the $x$ coordinate is much larger than that along the $y$ coordinate ($W \gg 2H$)
2. Continuity equation

\[ \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0 \Rightarrow \frac{\partial v_z}{\partial z} = 0 \]  
(Eq. 5-1)

3. Navier-Stokes equations in rectangular coordinates

In \( x \) direction,

\[ \rho \left[ \frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right] = -\frac{\partial P}{\partial x} + \mu \left[ \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right] + \rho g_x \]  
(Eq. 5-2)

In \( y \) direction,

\[ \rho \left[ \frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \right] = -\frac{\partial P}{\partial y} + \mu \left[ \frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_y}{\partial z^2} \right] + \rho g_y \]  
(Eq. 5-3)

In \( z \) direction,

\[ \rho \left[ \frac{\partial v_z}{\partial t} + v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \right] = -\frac{\partial P}{\partial z} + \mu \left[ \frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} + \frac{\partial^2 v_z}{\partial z^2} \right] + \rho g_z \]  
(Eq. 5-4)

After applying assumptions,

\[ \frac{\partial P}{\partial z} = \mu \frac{\partial^2 v_z}{\partial y^2}, \frac{\partial P}{\partial x} = 0, \frac{\partial P}{\partial y} = 0 \]  
(Eq. 5-5)

4. Boundary conditions:

\[ @ \; z = 0, P = P_0 \quad @ \; z = L, P = P_L \]

\[ @ \; y = 0, \frac{\partial v_z}{\partial y} = 0 \quad @ \; y = \frac{H}{2}, v_z = 0 \]  
(Eq. 5-6)

The expression of the velocity profile would be

\[ v_z (y) = \frac{P_L - P_0}{\mu L} \frac{y^2 - H^2}{2} \]  
(Eq. 5-7)
5. Numerical simulation

To simulate the fluid flow in the reactor channel, a physical model called “Laminar Flow” is used in COMSOL Multiphysics. The inlet is specified on the purple surface in Figure 86, and the inlet flow rate is defined. The outlet is designated on the red surface in Figure 86, and the outlet pressure is defined as the atmospheric pressure.

The result of numerical simulation for the momentum balance is illustrated below in Figure 87, Figure 89, Figure 91 and Figure 93. Figure 87 is the velocity contour in the 3D reaction channel, which shows the flow pattern in the reaction channel. Figure 89 is the velocity profile on the cut line shown in Figure 88 at the inlet on the y-z cut plane in the middle of x coordinate. The parabolic shape of this profile matches (Eq. 5-7) and proves the laminar flow. Figure 91 is the velocity profile on the cut line shown in Figure 90 at the inlet on the y-z cut plane in the middle of x coordinate. Figure 93 is the velocity profile on the cut line shown in Figure 92 at the outlet on the y-z cut plane in the middle of x coordinate. Since there is no velocity change along x coordinate and there is no slip on the wall, the velocity is zero at the wall and remains constant in the other section.

Besides, the average velocities on the inlet and outlet surfaces are measured, respectively 1.578m/s and 1.581m/s. Since the dimensions of these two surfaces are the same, it is reasonable that these two velocities are almost equal. Figure 89 illustrates the maximum velocity of 2.421m/s, which is around 1.5 times of the average velocity. This result matches the relationship between maximum velocity and average velocity in the laminar flow. Finally, the maximum Reynolds number in the whole reactor cell is 1.30, which is much smaller than 2000. This result also confirms the assumption of laminar flow.
Figure 87. Velocity Contour in 3D Reaction Channel

Figure 88. Cut Line at the Inlet on the y-z Cut Plane in the Middle of x Coordinate
Figure 89. Velocity Profile on the Cut Line at the Inlet on the y-z Cut Plane in the Middle of x Coordinate

Figure 90. Cut Line at the Inlet on the z-x Cut Plane in the Middle of y Coordinate
Figure 91. Velocity Profile on the Cut Line at the Inlet on the z-x Cut Plane in the Middle of y Coordinate

Figure 92. Cut Line at the Outlet on the z-x Cut Plane in the Middle of y Coordinate
5.2.2 Material Balance

1. Assumptions:

(1) No convection in y direction, \( v_y = 0 \)

(2) No convection or diffusion in x direction, \( v_x = 0, j_{i,x} = 0 \)

(3) Steady state process, \( \frac{w_i|_{t,\Delta t} - w_i|_{t}}{\Delta t} = 0 \)

(4) The temperature difference in the whole reactor cell can be neglected, \( \nabla T = 0 \)

2. Material balance governing equation

Governing equation: \( \text{IN} - \text{OUT} + \text{GENERATION} = \text{ACCUMULATION} \)
\[ v_x \cdot \rho w_i \cdot \Delta y \Delta z \Delta t \big|_{x+\Delta x} - v_x \cdot \rho w_i \cdot \Delta y \Delta z \Delta t \big|_{x} \]

Convection In – Convection Out: 
\[ + v_y \cdot \rho w_i \cdot \Delta x \Delta z \Delta t \big|_{y} - v_y \cdot \rho w_i \cdot \Delta x \Delta z \Delta t \big|_{y+\Delta y} \]
\[ + v_z \cdot \rho w_i \cdot \Delta x \Delta y \Delta t \big|_{z} - v_z \cdot \rho w_i \cdot \Delta x \Delta y \Delta t \big|_{z+\Delta z} \]

Diffusion In – Diffusion Out: 
\[ + j_{i,x} \cdot \Delta y \Delta z \Delta t \big|_{x} - j_{i,x} \cdot \Delta y \Delta z \Delta t \big|_{x+\Delta x} \]

Generation: 
\[ + R_i \cdot \Delta x \Delta y \Delta z \Delta t \]

Accumulation: 
\[ = \rho w_i \cdot \Delta x \Delta y \Delta z \big|_{i+\Delta t} - \rho w_i \cdot \Delta x \Delta y \Delta z \big|_{i} \]

After the simplification, the material balance becomes:
\[ v_z \cdot \rho w_i \cdot \Delta x \Delta y \Delta t \big|_{z} - v_z \cdot \rho w_i \cdot \Delta x \Delta y \Delta t \big|_{z+\Delta z} + j_{i,y} \cdot \Delta x \Delta z \Delta t \big|_{y+\Delta y} - j_{i,y} \cdot \Delta x \Delta z \Delta t \big|_{y} + j_{i,z} \cdot \Delta x \Delta y \Delta t \big|_{z+\Delta z} - j_{i,z} \cdot \Delta x \Delta y \Delta t \big|_{z} + R_i \cdot \Delta x \Delta y \Delta z \Delta t = 0 \]

(Eq. 5-8)

Divide by \( \Delta x \Delta y \Delta z \Delta t \), and take the limit as they approach zero:
\[ -\rho v_z \frac{\partial w_i}{\partial z} - \frac{\partial j_{i,y}}{\partial y} - \frac{\partial j_{i,z}}{\partial z} + R_i = 0 \]

(Eq. 5-9)

3. Mixture-averaged flux equation for a concentrated solution:
\[ j_i = - \left( \rho D_i^m \nabla w_i + \rho w_i D_i^m \frac{\nabla M_n}{M_n} + D_i^T \frac{\nabla T_f}{T_f} \right), \quad D_i^m = \frac{1 - w_i}{\sum_{k=1}^{3} \frac{x_k}{D_{ik}}}, \quad M_n = \frac{1}{\sum_{i} \frac{w_i}{M_i}} \]

(Eq. 5-10)

where \( j_i \) is mass flux vector, \( \text{kg}/(m^2 \cdot \text{sec}) \);
\( \rho \) is the density of the flow, \( \text{g}/\text{cm}^3 \);
\( D_i^m \) is the mixture-averaged diffusion coefficient, \( m^2/\text{sec} \);
\( D_{ik} \) is the multicomponent Maxwell-Stefan diffusivities, \( m^2/\text{sec} \), see Appendix E;
$w_i$ is the mass fraction of component $i$;

$x_k$ is the mole fraction of component $k$;

$M_n$ is the average molar mass of the mixture, $g/mol$;

$M_i$ is the molar mass of component $i, g/mol$;

$D_i^T$ is the thermal diffusion coefficient, $kg/(m\cdot sec)$;

$T_f$ is the temperature of the fluid, $K$.

After combination and simplification,

In $y$ direction

$$j_{i,y} = -\rho \left( \sum_{k \neq i} \frac{x_k}{D_{ik}} \frac{\partial}{\partial y} w_i + \sum_{k \neq i} \frac{x_k}{D_{ik}} \frac{w_i}{M_i} \frac{\partial}{\partial y} \sum_{i} \frac{w_i}{M_i} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) \left( \sum_{k \neq i} \frac{x_k}{D_{ik}} \frac{\partial}{\partial y} w_i + \sum_{k \neq i} \frac{x_k}{D_{ik}} \frac{w_i}{M_i} \frac{\partial}{\partial y} \sum_{i} \frac{w_i}{M_i} + \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) \right)$$

(Eq. 5-11)

$$\frac{\partial j_{i,y}}{\partial y} = \rho \left( \sum_{k \neq i} \frac{x_k}{D_{ik}} \frac{\partial^2 w_i}{\partial y^2} - (2w_i - 1) \frac{1}{\sum_{i} w_i} \frac{\partial w_i}{\partial y} + \frac{1}{\sum_{i} w_i^2} \frac{\partial^2 w_i}{\partial y^2} \right)$$

(Eq. 5-12)

In $z$ direction, similarly

$$\frac{\partial j_{i,z}}{\partial z} = \rho \left( \sum_{k \neq i} \frac{x_k}{D_{ik}} \frac{\partial^2 w_i}{\partial z^2} - (2w_i - 1) \frac{1}{\sum_{i} w_i} \frac{\partial w_i}{\partial z} + \frac{1}{\sum_{i} w_i^2} \frac{\partial^2 w_i}{\partial z^2} \right)$$

(Eq. 5-13)
Combine (Eq. 5-9), (Eq. 5-12) and (Eq. 5-13) to develop a partial differential expression for mass fraction \( w_i \):

\[
-\rho v_i \frac{\partial w_i}{\partial z} - \rho \sum_{k=1}^{n} \frac{x_k}{D_{ik}} \left[ w_i \left( \frac{\partial^2 w_i}{\partial y^2} - (2w_i - 1) \frac{\partial w_i}{\partial y} + \left( w_i^2 - w_i \right) \frac{\partial w_i}{\partial y} - \left( w_i^2 - w_i \right) \frac{\partial^2 w_i}{\partial y^2} \right) \right] \\
- \rho \sum_{k=1}^{n} \frac{x_k}{D_{ik}} \left[ w_i \frac{\partial^2 w_i}{\partial z^2} - (2w_i - 1) \frac{\partial w_i}{\partial z} + \left( w_i^2 - w_i \right) \frac{\partial w_i}{\partial z} - \left( w_i^2 - w_i \right) \frac{\partial^2 w_i}{\partial z^2} \right] + R_i = 0
\]

(Eq. 5-14)

4. Boundary conditions:

\[
\begin{align*}
@ y = 0, & \quad \frac{\partial w_i}{\partial y} (0, z) = 0 \\
@ y = H, & \quad \frac{\partial w_i}{\partial y} (H, z) = 0 \\
@ z = 0, w_i (y, 0) = w_{i,0} & \quad @ z = L, \frac{\partial w_i}{\partial z} (y, L) = 0
\end{align*}
\]

(Eq. 5-15)

5. Numerical simulation

To simulate the mass transfer in the reactor channel, a physical model called “Transport of Concentrated Species” has been used. The inflow is specified on the purple surface in Figure 86, and the molar concentrations of reactants are defined. The outflow is designated on the red surface in Figure 86. Reaction rates of reactants and products are defined in the activated discharge region, the highlighted part in Figure 94 while the reaction rates of reactants and products are set to zero at the remaining section. The remaining surfaces are specified as no flux. The results of numerical simulation of material balance are illustrated in Section 5.3 together with the numerical results of kinetics development.
Figure 94. Activated Discharge Region in the Modeling Subject

5.3 Kinetics Development

1. Mechanism of reactions

The pertinent chemical reaction equations describing the consumption of reactants and production of products are summarized as below.

\[
CO_2 + e^- \xrightleftharpoons{\kappa} CO^* + O^* + e^- \quad \text{(Eq. 5-16)}
\]

\[
CO^* \xrightarrow{\kappa_1} CO \quad \text{(Eq. 5-17)}
\]

\[
2O^* \xrightarrow{\kappa_1} O_2 \quad \text{(Eq. 5-18)}
\]

\[
H_2O + e^- \xrightarrow{\kappa_4} OH^* + H^* + e^- \quad \text{(Eq. 5-19)}
\]

\[
CO^* + e^- \xrightarrow{\kappa_3} C^* + O^* + e^- \quad \text{(Eq. 5-20)}
\]

\[
H^* + O^* \xrightarrow{\kappa_6} OH^* \quad \text{(Eq. 5-21)}
\]

\[
H^* + OH^* \xrightarrow{\kappa_1} H_2O \quad \text{(Eq. 5-22)}
\]

\[
C^* + H^* \xrightarrow{\kappa_5} CH^* \quad \text{(Eq. 5-23)}
\]
\[ CH^* + H^* \xrightarrow{k_b} CH_2^* \]  
(Eq. 5-24)

\[ CH_2^* + H^* \xrightarrow{k_b} CH_3^* \]  
(Eq. 5-25)

\[ CH_3^* + H^* \xrightarrow{k_b} CH_4 \]  
(Eq. 5-26)

2. Reaction rates of all the components:

\[ R_{CO} = \frac{dC_{CO}}{dt} = -k_1 C_{CO} C_{e^*} \]  
(Eq. 5-27)

\[ R_{H_2O} = \frac{dC_{H_2O}}{dt} = -k_4 C_{H_2O} C_{e^*} + k_7 C_{H^*} C_{OH^*} \]  
(Eq. 5-28)

\[ R_{CO} = \frac{dC_{CO}}{dt} = k_2 C_{CO^*} \]  
(Eq. 5-29)

\[ R_{O_2} = \frac{dC_{O_2}}{dt} = k_3 C_{O^2} \]  
(Eq. 5-30)

\[ R_{CH_4} = \frac{dC_{CH_4}}{dt} = k_{11} C_{CH^*} C_{H^*} \]  
(Eq. 5-31)

\[ R_{CO^*} = \frac{dC_{CO^*}}{dt} = k_5 C_{CO_2} C_{e^*} - k_2 C_{CO^*} - k_5 C_{CO^*} C_{e^*} \]  
(Eq. 5-32)

\[ R_{O^*} = \frac{dC_{O^*}}{dt} = k_5 C_{CO_2} C_{e^*} - k_5 C_{CO} C_{e^*} + k_3 C_{O^*} C_{e^*} - k_5 C_{H^*} C_{O^*} \]  
(Eq. 5-33)

\[ R_e = \frac{dC_e}{dt} = k_4 C_{CO_2} C_{e^*} + k_4 C_{H_2O} C_{e^*} + k_3 C_{CO^*} C_{e^*} \]  
(Eq. 5-34)

\[ R_{e^*} = \frac{dC_{e^*}}{dt} = k_5 C_{CO_2} C_{e^*} - k_6 C_{e^*} C_{H^*} \]  
(Eq. 5-35)

\[ R_{H^*} = \frac{dC_{H^*}}{dt} = k_4 C_{H_2O} C_{e^*} - k_6 C_{O^*} C_{H^*} - k_7 C_{OH^*} C_{H^*} - k_8 C_{e^*} C_{H^*} - k_3 C_{CH^*} C_{H^*} - k_{10} C_{CH^*} C_{H^*} - k_{11} C_{CH^*} C_{H^*} \]  
(Eq. 5-36)
\[ R_{\text{OH}}' = \frac{dC_{\text{OH}}'}{dt} = k_6 C_{\text{O}}' C_{\text{H}}' - k_7 C_{\text{OH}}' C_{\text{H}}' \] (Eq. 5-37)

\[ R_{\text{CH}}' = \frac{dC_{\text{CH}}'}{dt} = k_8 C_{\text{C}}' C_{\text{H}}' - k_9 C_{\text{CH}}' C_{\text{H}}' \] (Eq. 5-38)

\[ R_{\text{CH}_2} = \frac{dC_{\text{CH}_2}}{dt} = k_9 C_{\text{CH}}' C_{\text{H}}' - k_{10} C_{\text{CH}_2} C_{\text{H}}' \] (Eq. 5-39)

\[ R_{\text{CH}_3} = \frac{dC_{\text{CH}_3}}{dt} = k_{10} C_{\text{CH}_2} C_{\text{H}}' - k_{11} C_{\text{CH}_3} C_{\text{H}}' \] (Eq. 5-40)

3. Assumptions:

(1) If a Quasi-Steady-State assumption is invoked, the concentrations of all radicals are constant for all the radical-generation reactions.

\[
\frac{dC_{\text{CO}}'}{dt} = \frac{dC_{\text{C}}'}{dt} = \frac{dC_{\text{CH}}'}{dt} = \frac{dC_{\text{OH}}'}{dt} = \frac{dC_{\text{CH}_2}}{dt} = \frac{dC_{\text{CH}_3}}{dt} = 0
\]

(2) Assume \( n = \frac{k_5 C_{\text{CO}}' C_{\text{C}_v}}{k_2 C_{\text{CO}}'} \)

4. Simplifications

\[
\begin{align*}
R_{\text{CO}}' &= k_1 C_{\text{CO}}' C_{\text{C}_v} - k_2 C_{\text{CO}}' - k_3 C_{\text{CO}}' C_{\text{C}_v} = 0 \\
\Rightarrow \quad \begin{cases} 
  k_2 C_{\text{CO}}' = \frac{1}{n+1} k_1 C_{\text{CO}}' C_{\text{C}_v} \\
  k_3 C_{\text{CO}}' C_{\text{C}_v} = \frac{n}{n+1} k_1 C_{\text{CO}}' C_{\text{C}_v}
\end{cases}
\end{align*}
\] (Eq. 5-41)

\[
\begin{align*}
R_{\text{C}}' &= k_5 C_{\text{C}}' C_{\text{C}_v} - k_8 C_{\text{C}}' C_{\text{H}}' = 0 \\
R_{\text{CH}}' &= k_8 C_{\text{C}}' C_{\text{H}}' - k_9 C_{\text{CH}}' C_{\text{H}}' = 0 \\
R_{\text{CH}_2} &= k_9 C_{\text{CH}}' C_{\text{H}}' - k_{10} C_{\text{CH}_2} C_{\text{H}}' = 0 \\
R_{\text{CH}_3} &= k_{10} C_{\text{CH}_2} C_{\text{H}}' - k_{11} C_{\text{CH}_3} C_{\text{H}}' = 0
\end{align*}
\] (Eq. 5-42)
The reaction rates of reactants and products can be expressed as follow:

\[ R_{H_2O} = k_1 C_{H_2O} C_{\epsilon^2} - k_6 C_{\epsilon^2} C_{H_2O} - k_7 C_{OH} C_{H^-} - k_8 C^- C_{H^-} - k_9 C_{CH^2} C_{H^-} - k_{10} C_{CH^2} C_{H^-} - k_{11} C_{CH^2} C_{H^-} = 0 \]

\[ R_{OH} = k_6 C_{\epsilon^2} C_{H^-} - k_7 C_{OH} C_{H^-} = 0 \]

\[ k_8 C^- C_{H^-} = k_9 C_{CH^2} C_{H^-} = k_{10} C_{CH^2} C_{H^-} = k_{11} C_{CH^2} C_{H^-} = \frac{n}{n+1} k_4 C_{H_2O} C_{\epsilon^2} \]

\[ \Rightarrow k_7 C_{\epsilon^2} C_{OH} = \frac{k_4 C_{H_2O} C_{\epsilon^2}}{2} - \frac{2n}{n+1} k_3 C_{CO} C_{\epsilon^2} \]

(Eq. 5-43)

\[ R_{CO} = k_3 C_{CO} C_{\epsilon^2} - k_5 C_{\epsilon^2}^2 + k_5 C_{CO} C_{\epsilon^2} - k_8 C_{\epsilon^2} C_{O^-} = 0 \]

\[ k_5 C_{CO} C_{\epsilon^2} = \frac{n}{n+1} k_1 C_{CO} C_{\epsilon^2} \]

\[ R_{OH} = k_8 C_{\epsilon^2} C_{H^-} - k_7 C_{OH} C_{H^-} = 0 \]

\[ k_7 C_{\epsilon^2} C_{OH} = \frac{k_4 C_{H_2O} C_{\epsilon^2}}{2} - \frac{2n}{n+1} k_3 C_{CO} C_{\epsilon^2} \]

\[ \Rightarrow k_3 C_{\epsilon^2} = \frac{4n+1}{n+1} k_1 C_{CO} C_{\epsilon^2} - \frac{k_4 C_{H_2O} C_{\epsilon^2}}{2} \]

(Eq. 5-44)

The reaction rates of reactants and products can be expressed as follow:

\[ R_{CO} = -k_1 C_{CO} C_{\epsilon^2} \]

(Eq. 5-45)

\[ R_{H_2O} = -k_4 C_{H_2O} C_{\epsilon^2} + k_7 C_{\epsilon^2} C_{OH} \]

\[ k_7 C_{\epsilon^2} C_{OH} = \frac{k_4 C_{H_2O} C_{\epsilon^2}}{2} - \frac{2n}{n+1} k_3 C_{CO} C_{\epsilon^2} \]

\[ \Rightarrow R_{H_2O} = -\frac{k_4 C_{H_2O} C_{\epsilon^2}}{2} - \frac{2n}{n+1} k_3 C_{CO} C_{\epsilon^2} \]

(Eq. 5-46)

\[ R_{CO} = k_2 C_{CO} = \frac{1}{n+1} k_1 C_{CO} C_{\epsilon^2} \]

(Eq. 5-47)

\[ R_{O_2} = \frac{dC_{O_2}}{dt} = k_3 C_{O_2}^2 \]

\[ k_3 C_{O_2}^2 = \frac{4n+1}{n+1} k_1 C_{CO} C_{\epsilon^2} - \frac{k_4 C_{H_2O} C_{\epsilon^2}}{2} \]

\[ \Rightarrow R_{O_2} = \frac{4n+1}{n+1} k_1 C_{CO} C_{\epsilon^2} - \frac{k_4 C_{H_2O} C_{\epsilon^2}}{2} \]

(Eq. 5-48)
There are three variables related to the reaction kinetics: $k_1$, $k_4$, and $n$. The kinetics is mainly influenced by the excitation of electrons rather than the vibration of molecules in the corona discharge involved reaction process. Therefore, $k_1$ and $k_4$ can be expressed in the modified Arrhenius equation as shown below:

$$k = k_0 \cdot \exp \left( -\frac{E_A}{\beta V e} \right)$$  \hspace{1cm} \text{(Eq. 5-50)}$$

The activation energies for $k_1$ and $k_4$ are respectively $+5.58$ eV$^{23}$ and $+3.74$ eV$^{75}$. Since the current ($I$), the voltage across the reactor ($V$) and Faraday constant ($F$) are known, the only variables in (Eq. 5-50) are $k_0$ and $\beta$. Besides, to combine with the mass balance equation, reaction rates need to be expressed in mass fractions. Therefore, the final expressions of reaction rates are

$$R_{CO_2} = -k_{0,1} \cdot e^{\frac{E_{A,i}}{\beta V e}} w_{CO_2} M_{CO_2} \cdot \frac{I \cdot t_{\text{electron}}}{F \cdot V_{\text{active}}}$$  \hspace{1cm} \text{(Eq. 5-51)}$$

$$R_{H_2O} = -\frac{k_{0,4} \cdot e^{\frac{E_{A,i}}{\beta V e}} w_{H_2O} M_{H_2O} \cdot \frac{I \cdot t_{\text{electron}}}{F \cdot V_{\text{active}}}}{2} - \frac{2n}{n+1} k_{0,1} \cdot e^{\frac{E_{A,i}}{\beta V e}} w_{CO_2} M_{CO_2} \cdot \frac{I \cdot t_{\text{electron}}}{F \cdot V_{\text{active}}}$$  \hspace{1cm} \text{(Eq. 5-52)}$$

$$R_{CO} = \frac{1}{n+1} k_{0,1} \cdot e^{\frac{E_{A,i}}{\beta V e}} w_{CO_2} M_{CO_2} \cdot \frac{I \cdot t_{\text{electron}}}{F \cdot V_{\text{active}}}$$  \hspace{1cm} \text{(Eq. 5-53)}$$

$$R_{O_2} = \frac{4n+1}{n+1} k_{0,1} \cdot e^{\frac{E_{A,i}}{\beta V e}} w_{CO_2} M_{CO_2} \cdot \frac{I \cdot t_{\text{electron}}}{F \cdot V_{\text{active}}} - \frac{k_{0,4} \cdot e^{\frac{E_{A,i}}{\beta V e}} w_{H_2O} M_{H_2O} \cdot \frac{I \cdot t_{\text{electron}}}{F \cdot V_{\text{active}}}}{2}$$  \hspace{1cm} \text{(Eq. 5-54)}$$

$$R_{CH_4} = \frac{n}{n+1} k_{0,1} \cdot e^{\frac{E_{A,i}}{\beta V e}} w_{CO_2} M_{CO_2} \cdot \frac{I \cdot t_{\text{electron}}}{F \cdot V_{\text{active}}}$$  \hspace{1cm} \text{(Eq. 5-55)}$$
where $R_{CO_2}$, $R_{H_2O}$, $R_{CO}$, $R_{O_2}$ and $R_{CH_4}$ = reaction rate of CO$_2$, H$_2$O, CO, O$_2$ and CH$_4$, unit: g/(m$^3$·sec);

$k_{0,1}, k_{0,4}$ = pre-exponential factor for dissociation of CO$_2$ and H$_2$O, unit: sec$^{-1}$;

$E_{A,1}, E_{A,4}$ = activation energy for dissociation of CO$_2$ and H$_2$O, unit: eV;

$\beta_1, \beta_4$ = exponential kinetic parameter for dissociation of CO$_2$ and H$_2$O, unit: dimensionless;

$V$ = voltage across the reactor, unit: V;

$F$ = Faraday constant, $F$ = 96485C/mol;

$w_{CO_2}, w_{H_2O}$ = mass fraction of CO$_2$ and H$_2$O, unit: dimensionless;

$M_{CO_2}, M_{H_2O}$ = molecular mass of CO$_2$ and H$_2$O, unit: g/mol;

$n$ = kinetic parameter that decides the production pathway to CO or CH$_4$, unit: dimensionless;

$I$ = current through the reactor, unit: A;

$t_{\text{electron}}$ = time that activated electrons travel through the gap, unit: sec;

$V_{\text{active}}$ = active volume for reaction, unit: m$^3$.

Five kinetics related variables need to be extracted through the optimization are: $k_{0,1}$, $\beta_1$, $k_{0,4}$, $\beta_4$ and $n$.

5. Numerical simulation

In the physical model “Transport of Concentrated Species”, reaction rates of reactants and products are defined as the expressions in (Eq. 5-51) to (Eq. 5-55). The result of numerical simulation for the material balance and kinetics is illustrated below in Figure 95 and Figure 97. Figure 95 is the concentration contour in the 3D reaction channel, which shows the concentration pattern in the reaction channel. In Figure 97, the concentration profiles of reactants and products are plotted on the cut line shown in
**Figure 96** along the flow direction on the y-z cut plane in the middle of x coordinate. As illustrated in the concentration profiles, CO₂ and H₂O are consumed during the reaction process, so their concentrations steadily decline, and concentrations of products CO, CH₄ and O₂ continue to show upward tendencies along the reaction channel.

**Figure 95. Mass Fraction Contour in 3D Reaction Channel (Estimated Kinetic Parameters)**
Figure 96. Cut Line Along z Coordinate in the Middle of the y-z Cut Plane

Figure 97. Concentration Profiles of Reactants and Products on the Cut Line Along z Coordinate in the Middle of the y-z Cut Plane (Estimated Kinetic Parameters)
The overall mass balance for the fluid through the reactor and mass balance of all the chemical elements (C, H, and O) were checked, and the results are shown below in Table 3. The consistencies of the mass flow rates and mass fraction of all the chemical elements at inlet and outlet surfaces indicate a satisfying mass balance.

**Table 3. Mass Flow Rates and Mass Fraction of C, H, O at Inlet and Outlet Surface**

<table>
<thead>
<tr>
<th></th>
<th>Inlet</th>
<th>Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mass flow rate (g/sec)</strong></td>
<td>1.17×10⁻³</td>
<td>1.17×10⁻³</td>
</tr>
<tr>
<td><strong>Mass fraction of C</strong></td>
<td>14.90%</td>
<td>13.61%</td>
</tr>
<tr>
<td><strong>Mass fraction of H</strong></td>
<td>5.04%</td>
<td>4.32%</td>
</tr>
<tr>
<td><strong>Mass fraction of O</strong></td>
<td>80.06%</td>
<td>82.07%</td>
</tr>
</tbody>
</table>

Two tests on this numerical model were conducted. When there is no electrical current through the reactor, there should be no reaction happening in theory. That is to say, in the numerical model, reactants CO₂ and H₂O should keep constant at the inlet concentrations while the concentrations of all the products should remain at zero. The result of the numerical model with no voltage applied illustrated in Figure 98 agrees with the expectation. Another test is to set zero concentrations for reactants. Theoretically, there should be no reaction occurring either. In other words, the concentrations of all the species should be at zero. The result of the numerical model with no reactants illustrated in Figure 99 matches the expectation.
Figure 98. Concentration Profiles of Reactants and Products on the Cut Line Along $z$ Coordinate in the Middle of the $y$-$z$ Cut Plane with no Power

Figure 99. Concentration Profiles of Reactants and Products on the Cut Line Along $z$ Coordinate in the Middle of the $y$-$z$ Cut Plane with no Reactants
5.4 Kinetics Extraction through Optimization of Numerical Model

To obtain the reaction rate constants, higher level numerical operations need to be done: optimization of the numerical model. The COMSOL-Matlab LiveLink is used for this operation. **Figure 100** is the scheme of the concept for this operation. First, initial guesses of kinetic parameters need to be input for the numerical model, and simulated results of concentrations can be obtained. Then, the objective function can be calculated using simulated concentrations and experimental concentrations following the equation below:

\[
\text{Objective Function } F_{\text{obj}} = \sum_{i=1}^{n} W_i \left( C_{i,\text{mod}} - C_{i,\text{exp}} \right)^2
\]

(Eq. 5-56)

Next, the software varies the values of the kinetic parameters based on Nelder-Mead simplex algorithm to obtain the minimum of the absolute value of the difference between initial and new objective function. If the absolute value of the difference between initial and new objective function is smaller than the pre-set tolerance, then the kinetic parameters in the new objective function would be the final results, otherwise, repeat the steps above until the results satisfy the requirement. The detailed procedures of this optimization operation are listed in Appendix G.
Figure 100. Scheme of Concept for the Optimization Process of Numerical Model

The kinetic parameters are obtained by fitting the numerical model to experimental data generated from the corona microreactor for CO₂ reduction process. As illustrated in Figure 101-103, the model predictions agree with experimental data after the extraction of the kinetic parameters. The kinetic parameters are listed in Table 4.
Figure 101. Comparison of Optimization Result and Experimental Data (Operation Points in Different Regimes of V-I Curve)

Figure 102. Comparison of Optimization Result and Experimental Data (Different Flow Rate of CO₂)
Sensitivity of the kinetic parameters can be calculated according to the fitting between simulated results and experimental data. Two outliers are observed out of 70 data points based on the confidence interval of 95%. The following equations are used for this calculation:

\[
\text{Sensitivity: } sens = \frac{TP}{TP + FN} = 97.143\% \quad \text{(Eq. 5-57)}
\]

\[
\text{Standard error: } SE = \sqrt{\frac{\text{sens}(1-\text{sens})}{TP + FN}} = 1.991\% \quad \text{(Eq. 5-58)}
\]

where TP = true positive test results, in this case TP = 68;

FN = false negative test results, in this case FN = 2;
Table 4. Kinetic Parameters and Reaction Rate Constants

<table>
<thead>
<tr>
<th>Kinetic Parameters</th>
<th>Value</th>
<th>Reaction Rate Constants</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{0,1}$ [sec$^{-1}$]</td>
<td>3.543±0.071×10$^{10}$</td>
<td>$k_{1}$ [sec$^{-1}$]</td>
<td>3.541×10$^{10}$</td>
</tr>
<tr>
<td>$\beta_1$ [1]</td>
<td>2.181±0.044×10$^{1}$</td>
<td>$k_{4}$ [sec$^{-1}$]</td>
<td>1.265×10$^{8}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0 when CO$_2$ only)</td>
</tr>
<tr>
<td>$k_{0,4}$ [sec$^{-1}$]</td>
<td>1.266±0.025×10$^{8}$ (0 when CO$_2$ only)</td>
<td>$n$ [1]</td>
<td>0.5 (0 when CO$_2$ only)</td>
</tr>
<tr>
<td>$\beta_4$ [1]</td>
<td>8.403±0.168</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$ [1]</td>
<td>0.5±0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0 when CO$_2$ only)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.5 Summary of Numerical Simulation and Optimization

The mathematical model was developed to describe the momentum balance, material balance and kinetics for the CO$_2$ reduction process in corona microreactor. A numerical model based on it was solved using COMSOL Multiphysics software program. The kinetics parameters were predicted by fitting the model to experimental data using COMSOL-Matlab LiveLink. It was found that the prediction result well-explained the experimental data, and it can be confidently concluded that the developed model for the microreactor type used in this study may be used to predict reduction of CO$_2$ under various operating conditions.

References

Chapter 6- Conclusions, Recommendations and Contribution to Science

6.1 Experimental and Modeling Results

It was determined through experiments that through-gas reactor configuration and needle-to-plate design are the suitable reactor design for CO$_2$ reduction process. Several microscale-based corona reactors were designed and manufactured to investigate the influence of the factors on the performance of the reactor and energy efficiency. These factors include active volume ratio, flow rate of CO$_2$, operation points in different regime of V-I curve, CO$_2$-to-H$_2$O molar ratio and the distribution of corona points. The conclusions can be made as below:

(1) Larger active volume ratio is helpful to improve the performance of the reactor and energy efficiency. An optimal design and a high quality of manufacturing are required to achieve this goal.

(2) It can be concluded that conversion of CO$_2$ is increasing with the decreasing flow rate of CO$_2$, but higher energy efficiency and reactor efficiency can be achieved at a higher flow rate of CO$_2$.

(3) The conversion of CO$_2$ is greater in glow regime than spark regime and arc regime, and it reaches the maximum in the glow regime with the highest current. The energy efficiency in the arc regime is much lower than glow regime and spark regime.

(4) The conversion of CO$_2$ is slightly higher with higher water content since it favors the forward reaction. The energy efficiency and reactor efficiency are higher when CO$_2$-to-H$_2$O molar ratio matches the ratio of stoichiometric numbers.

(5) Conversion of CO$_2$ and energy efficiency are higher when the flow direction is perpendicular to the distribution direction of corona points than parallel with the distribution direction.

The mathematical model was developed to describe the momentum balance, material balance and kinetics for the CO$_2$ reduction process in corona microreactor. A numerical model based on it was solved using COMSOL Multiphysics software program. The
kinetics parameters were predicted by fitting the model to experimental data using COMSOL-Matlab LiveLink. It was found that the prediction result explained the experimental results well, and it can be confidentially concluded that the developed model for the microreactor type used in this study may be used to predict reduction of CO₂ under various operating conditions.

6.2 Recommendations for Future Work

This research lays the foundation for more detailed studies focusing on CO₂ reduction in microscale-based multi-point DC corona discharge. There are four fundamental recommendations for continued research for CO₂ reduction in corona microreactors.

Future optimization of the flow path in the channels of microscale-based reactor cell should be pursued to reduce bypass limits which exist in the present systems. Two methods can be applied to reach this goal: (1) decreasing the bypass volume by reducing or eliminating the gap distances between needles; (2) increasing the active volume by narrowing the needle-to-needle distance.

Based on the preliminary data on dry reforming using corona discharge by Justin Pommerenck in the group, I hypothesize that a slower flow rate of CO₂ could induce the generation of longer chain hydrocarbon products, such as C₂, C₃, C₄ and so on, which are more useful and profitable than methane and carbon monoxide in the present products.

Other than DC corona discharge, there are some other kinds of non-thermal plasma, such as AC corona discharge and electromagnetic discharge. There is a chance that these plasmas can provide a better conversion and higher energy efficiency than corona discharge.

Further into the research, the industrial application should be considered. The “numbering-up” strategy can be applied to scale up the reactor system, which includes delivering reactant stream through multiple microreactors in series or parallel and arrangement of the power source for multiple reactors. The capacity will be enhanced due to the increasing volume of reactants and decreasing overall cost.
6.3 Contribution to Science

This study contributes to science by creating a fundamental designed microscale-based model for CO$_2$ reduction with the presence of corona discharge. This tool passed three primary tests (including global test, dynamic test, and local test) by the accomplishment of a balance of carbon element, proper operation and safe operation procedure. It also makes a contribution to science by producing the experimental data for CO$_2$ reduction with the presence of corona discharge and calculating the kinetic parameters, which can be used to predict reactions under similar conditions.
Appendix
A. Summary of Experimental Data

A-1. Multi-point Corona Reactor with 200-pin Plate

Table A-1. Experimental Data on Reactor with 200-pin for Different Flow Rate of CO₂ (Glow Regime, Voltage on Reactor = 0.87 kV, Current = 0.56 mA, mol(CO₂):mol(H₂O) = 1:2)

<table>
<thead>
<tr>
<th>Flow Rate of CO₂ (sccm)</th>
<th>Peak Area of CO₂</th>
<th>Peak Area of H₂O</th>
<th>Peak Area of O₂</th>
<th>Peak Area of CO</th>
<th>Peak Area of CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>312.9894</td>
<td>0.3055</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>20</td>
<td>310.1648</td>
<td>0.2998</td>
<td>1514.4092</td>
<td>1178.2645</td>
<td>1170.5238</td>
</tr>
<tr>
<td></td>
<td>310.1464</td>
<td>0.2997</td>
<td>1493.5324</td>
<td>1197.5432</td>
<td>1175.9064</td>
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<tr>
<td></td>
<td>310.1045</td>
<td>0.2999</td>
<td>1553.8543</td>
<td>1187.7345</td>
<td>1180.0634</td>
</tr>
<tr>
<td>30</td>
<td>310.5363</td>
<td>0.3006</td>
<td>1263.0530</td>
<td>1007.0942</td>
<td>1001.0431</td>
</tr>
<tr>
<td></td>
<td>310.4645</td>
<td>0.3004</td>
<td>1292.6320</td>
<td>1046.0433</td>
<td>1054.6543</td>
</tr>
<tr>
<td></td>
<td>310.3553</td>
<td>0.3003</td>
<td>1353.1210</td>
<td>1087.0653</td>
<td>1094.6093</td>
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<tr>
<td>50</td>
<td>311.0238</td>
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<td>311.0938</td>
<td>0.3017</td>
<td>1009.9842</td>
<td>780.6549</td>
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<td></td>
<td>311.0343</td>
<td>0.3018</td>
<td>990.0053</td>
<td>804.6437</td>
<td>829.6514</td>
</tr>
</tbody>
</table>

Table A-2. Data of Concentration on Reactor with 200-pin for Different Flow Rate of CO₂ (Glow Regime, Voltage on Reactor = 0.87 kV, Current = 0.56 mA, mol(CO₂):mol(H₂O) = 1:2)

<table>
<thead>
<tr>
<th>Flow Rate of CO₂ (sccm)</th>
<th>Concentration of CO₂ (µmol/ml)</th>
<th>Concentration of H₂O (µmol/ml)</th>
<th>Concentration of O₂ (µmol/ml)</th>
<th>Concentration of CO (µmol/ml)</th>
<th>Concentration of CH₄ (µmol/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>15.649</td>
<td>10.266</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>20</td>
<td>15.508</td>
<td>10.172</td>
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</tr>
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<td>0.064</td>
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</table>
Table A-3. Calculated Data on Reactor with 200-pin for Different Flow Rate of CO₂ (Glow Regime, Voltage on Reactor = 0.87kV, Current = 0.56mA, mol(CO₂):mol(H₂O) = 1:2)

<table>
<thead>
<tr>
<th>Flow Rate of CO₂ (sccm)</th>
<th>Conversion of CO₂ in Whole Reactor (%)</th>
<th>Conversion of CO₂ in Active Volume (%)</th>
<th>Energy Efficiency (%)</th>
<th>Reactor Efficiency (%)</th>
<th>Carbon Balance (µmol/ml)</th>
<th>Hydrogen Balance (µmol/ml)</th>
<th>Oxygen Balance (µmol/ml)</th>
<th>Selectivity CH₄/CO</th>
</tr>
</thead>
<tbody>
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<td>4.42</td>
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<td>0.497</td>
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<td>81.10</td>
<td>4.46</td>
<td>0.05</td>
<td>15.603</td>
<td>20.529</td>
<td>41.580</td>
<td>0.491</td>
</tr>
<tr>
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<td>41.590</td>
<td>0.497</td>
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<td>7.63</td>
<td>0.09</td>
<td>15.617</td>
<td>20.535</td>
<td>41.578</td>
<td>0.500</td>
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<tr>
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<td>54.08</td>
<td>7.39</td>
<td>0.08</td>
<td>15.617</td>
<td>20.537</td>
<td>41.578</td>
<td>0.520</td>
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<td>0.62</td>
<td>55.77</td>
<td>7.47</td>
<td>0.08</td>
<td>15.616</td>
<td>20.544</td>
<td>41.571</td>
<td>0.516</td>
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<td>7.63</td>
<td>0.09</td>
<td>15.617</td>
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<td>7.39</td>
<td>0.08</td>
<td>15.617</td>
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<td>41.578</td>
<td>0.520</td>
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<td>0.08</td>
<td>15.616</td>
<td>20.544</td>
<td>41.571</td>
<td>0.516</td>
</tr>
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</table>

Table A-4. Experimental Data on Reactor with 200-pin for Different Distribution of Corona Points (Glow Regime, Voltage on Reactor = 0.87kV, Current = 0.56mA, mol(CO₂):mol(H₂O) = 1:2, Flow Rate of CO₂ = 20 sccm)

<table>
<thead>
<tr>
<th>Plate Size</th>
<th>Peak Area of CO₂</th>
<th>Peak Area of H₂O</th>
<th>Peak Area of O₂</th>
<th>Peak Area of CO</th>
<th>Peak Area of CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
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<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Flow Parallel with</td>
<td>310.1648</td>
<td>0.2998</td>
<td>1514.4092</td>
<td>1178.2645</td>
<td>1170.5238</td>
</tr>
<tr>
<td>Distribution Direction</td>
<td>310.1464</td>
<td>0.2997</td>
<td>1493.5324</td>
<td>1197.5432</td>
<td>1175.9064</td>
</tr>
<tr>
<td></td>
<td>310.1045</td>
<td>0.2999</td>
<td>1553.8543</td>
<td>1187.7345</td>
<td>1180.0634</td>
</tr>
<tr>
<td>Flow Perpendicular to</td>
<td>309.7349</td>
<td>0.2990</td>
<td>1720.3436</td>
<td>1342.9679</td>
<td>1308.9034</td>
</tr>
<tr>
<td>Distribution Direction</td>
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<td>0.2992</td>
<td>1642.6423</td>
<td>1322.7793</td>
<td>1362.4628</td>
</tr>
<tr>
<td></td>
<td>309.9033</td>
<td>0.2993</td>
<td>1634.3659</td>
<td>1274.9652</td>
<td>1297.0123</td>
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</tbody>
</table>
## Table A-5. Data of Concentration on Reactor with 200-pin for Different Distribution of Corona Points (Glow Regime, Voltage on Reactor = 0.87kV, Current = 0.56mA, mol(CO2):mol(H2O) = 1:2, Flow Rate of CO2 = 20 sccm)

<table>
<thead>
<tr>
<th>Plate Size</th>
<th>Concentration of CO2 (µmol/ml)</th>
<th>Concentration of H2O (µmol/ml)</th>
<th>Concentration of O2 (µmol/ml)</th>
<th>Concentration of CO (µmol/ml)</th>
<th>Concentration of CH4 (µmol/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>15.649</td>
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<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Flow Parallel with Distribution</td>
<td>15.508</td>
<td>10.172</td>
<td>0.151</td>
<td>0.094</td>
<td>0.047</td>
</tr>
<tr>
<td>Direction</td>
<td>15.507</td>
<td>10.171</td>
<td>0.149</td>
<td>0.096</td>
<td>0.047</td>
</tr>
<tr>
<td>Flow Perpendicular to Distribution</td>
<td>15.505</td>
<td>10.174</td>
<td>0.155</td>
<td>0.095</td>
<td>0.047</td>
</tr>
</tbody>
</table>

## Table A-6. Calculated Data on Reactor with 200-pin for Comparison Between Full Plate and Half Plate (Glow Regime, Voltage on Reactor = 0.87kV, Current = 0.56mA, mol(CO2):mol(H2O) = 1:2, Flow Rate of CO2 = 20 sccm)

<table>
<thead>
<tr>
<th>Plate Size</th>
<th>Conversion of CO2 in Whole Reactor (%)</th>
<th>Conversion of CO2 in Active Volume (%)</th>
<th>Energy Efficiency (%)</th>
<th>Reactor Efficiency (%)</th>
<th>Carbon Balance (µmol/ml)</th>
<th>Hydrogen Balance (µmol/ml)</th>
<th>Oxygen Balance (µmol/ml)</th>
<th>Selectivity CH4/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
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</tr>
<tr>
<td>Flow Parallel with Distribution</td>
<td>0.90</td>
<td>80.58</td>
<td>4.42</td>
<td>0.05</td>
<td>15.603</td>
<td>20.532</td>
<td>41.586</td>
<td>0.497</td>
</tr>
<tr>
<td>Direction</td>
<td>0.91</td>
<td>81.10</td>
<td>4.46</td>
<td>0.05</td>
<td>15.603</td>
<td>20.529</td>
<td>41.580</td>
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</tr>
<tr>
<td></td>
<td>0.92</td>
<td>82.30</td>
<td>4.46</td>
<td>0.05</td>
<td>15.600</td>
<td>20.537</td>
<td>41.590</td>
<td>0.497</td>
</tr>
<tr>
<td>Flow Perpendicular to Distribution</td>
<td>1.04</td>
<td>92.84</td>
<td>5.09</td>
<td>0.06</td>
<td>15.594</td>
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<tr>
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<td>15.597</td>
<td>20.535</td>
<td>41.583</td>
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</tr>
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</table>
# A-2. Multi-point Corona Reactor with 100-pin Plate

Table A-7. Experimental Data on Reactor with 100-pin for Operation Points at Different Regimes on V-I Curve (Flow Rate of CO\(_2\) = 50 sccm, mol(CO\(_2\)) : mol(H\(_2\)O) = 1:2)

<table>
<thead>
<tr>
<th>Regime</th>
<th>V(_{\text{reactor}}) (kV)</th>
<th>Current (mA)</th>
<th>Peak Area of CO(_2)</th>
<th>Peak Area of H(_2)O</th>
<th>Peak Area of O(_2)</th>
<th>Peak Area of CO</th>
<th>Peak Area of CH(_4)</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>406.3021</td>
<td>163.9021</td>
<td>4094.8432</td>
<td>2757.7630</td>
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<tr>
<td>Glow Regime</td>
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<td>395.9699</td>
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<td>6990.0123</td>
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<tr>
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</table>
Table A-8. Data of Concentration on Reactor with 100-pin for Operation Points at Different Regimes on V-I Curve (Flow Rate of CO₂ = 50 sccm, mol(CO₂):mol(H₂O) = 1:2)

<table>
<thead>
<tr>
<th>Regime</th>
<th>V-reactor (kV)</th>
<th>Current (mA)</th>
<th>Concentration of CO₂ (µmol/ml)</th>
<th>Concentration of H₂O (µmol/ml)</th>
<th>Concentration of O₂ (µmol/ml)</th>
<th>Concentration of CO (µmol/ml)</th>
<th>Concentration of CH₄ (µmol/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
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<td>20.649</td>
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<tr>
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<td>41.692</td>
<td>0.409</td>
<td>0.221</td>
<td>0.111</td>
</tr>
<tr>
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<td>41.443</td>
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<td>0.560</td>
<td>0.280</td>
</tr>
<tr>
<td>Regime</td>
<td></td>
<td></td>
<td>19.773</td>
<td>41.441</td>
<td>0.806</td>
<td>0.584</td>
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Table A-9. Calculated Data on Reactor with 100-pin for Operation Points at Different Regimes on V-I Curve (Flow Rate of CO\textsubscript{2} = 50 sccm, mol(CO\textsubscript{2}):mol(H\textsubscript{2}O) = 1:2)

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<th>Conversion of CO\textsubscript{2} in Active Volume (%)</th>
<th>Energy Efficiency (%)</th>
<th>Reactor Efficiency (%)</th>
<th>Carbon Balance (µmol/ml)</th>
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Table A-10. Experimental Data on Reactor with 100-pin for Different Flow Rate of CO$_2$ (Glow Regime, Voltage on Reactor = 0.814kV, Current = 0.42mA, mol(CO$_2$):mol(H$_2$O) = 1:2)

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<th>Peak Area of O$_2$</th>
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Table A-11. Data of Concentration on Reactor with 100-pin for Different Flow Rate of CO$_2$ (Glow Regime, Voltage on Reactor = 0.814kV, Current = 0.42mA, mol(CO$_2$):mol(H$_2$O) = 1:2)

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<th>Concentration of H$_2$O (µmol/ml)</th>
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Table A-12. Calculated Data on Reactor with 100-pin for Different Flow Rate of CO\textsubscript{2} (Glow Regime, Voltage on Reactor = 0.814kV, Current = 0.42mA, mol(CO\textsubscript{2}):mol(H\textsubscript{2}O) = 1:2)

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<th>Conversion of CO\textsubscript{2} in Active Volume (%)</th>
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<th>Reactor Efficiency (%)</th>
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<td>10.68</td>
<td>20.358</td>
<td>84.004</td>
<td>83.212</td>
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</tr>
<tr>
<td></td>
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<td>10.68</td>
<td>20.362</td>
<td>84.026</td>
<td>83.214</td>
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</tr>
<tr>
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<td>22.22</td>
<td>98.08</td>
<td>11.67</td>
<td>20.467</td>
<td>83.815</td>
<td>83.591</td>
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</tr>
<tr>
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<td>83.822</td>
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<td>11.67</td>
<td>20.468</td>
<td>83.837</td>
<td>83.585</td>
<td>0.504</td>
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<tr>
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<td>2.64</td>
<td>22.22</td>
<td>98.08</td>
<td>11.67</td>
<td>20.467</td>
<td>83.815</td>
<td>83.591</td>
<td>0.495</td>
</tr>
</tbody>
</table>
Table A-13. Experimental Data on Reactor with 100-pin for Different CO$_2$ to H$_2$O Ratio (Glow Regime, Voltage on Reactor = 0.814kV, Current = 0.42mA, Flow Rate of CO$_2$ = 50 scm)

<table>
<thead>
<tr>
<th>CO$_2$ to H$_2$O Molar Ratio</th>
<th>Flow Rate of H$_2$O (ml/min)</th>
<th>Peak Area of CO$_2$</th>
<th>Peak Area of H$_2$O</th>
<th>Peak Area of O$_2$</th>
<th>Peak Area of CO</th>
<th>Peak Area of CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank (1:2)</td>
<td>0.081</td>
<td>412.9894</td>
<td>171.2855</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1:2</td>
<td>0.081</td>
<td>395.9699</td>
<td>155.9362</td>
<td>8063.0710</td>
<td>6997.0320</td>
<td>6990.0123</td>
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<tr>
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<td>0.081</td>
<td>395.4665</td>
<td>155.8734</td>
<td>8062.9720</td>
<td>7296.8310</td>
<td>7299.9721</td>
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<tr>
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<td>0.081</td>
<td>395.8901</td>
<td>156.0011</td>
<td>8063.1210</td>
<td>7097.1410</td>
<td>7101.0732</td>
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<tr>
<td>Blank (3:2)</td>
<td>0.027</td>
<td>442.0243</td>
<td>0.9023</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>3:2</td>
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<td>424.0890</td>
<td>0.8092</td>
<td>9292.0540</td>
<td>7400.4320</td>
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<tr>
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<td>0.027</td>
<td>424.0543</td>
<td>0.8083</td>
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<td>7406.6530</td>
<td>7535.0564</td>
</tr>
<tr>
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<td>424.0342</td>
<td>0.8099</td>
<td>9305.6530</td>
<td>7435.5410</td>
<td>7553.0650</td>
</tr>
<tr>
<td>Blank (2:1)</td>
<td>0.020</td>
<td>402.9054</td>
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<td>0.0000</td>
</tr>
<tr>
<td>2:1</td>
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<td>386.9648</td>
<td>0.2609</td>
<td>8034.4330</td>
<td>6643.4350</td>
<td>6642.4370</td>
</tr>
<tr>
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<td>0.020</td>
<td>387.0324</td>
<td>0.2611</td>
<td>8024.4320</td>
<td>6654.4320</td>
<td>6602.6530</td>
</tr>
<tr>
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<td>0.020</td>
<td>386.9923</td>
<td>0.2610</td>
<td>8036.4750</td>
<td>6643.5370</td>
<td>6623.4630</td>
</tr>
<tr>
<td>Blank (CO$_2$ only)</td>
<td></td>
<td>435.3267</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
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<tr>
<td>CO$_2$ only</td>
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<td>418.5432</td>
<td>4432.6840</td>
<td>11023.8520</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
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<td></td>
<td>418.5324</td>
<td>4474.4740</td>
<td>11034.6430</td>
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<td>0.0000</td>
</tr>
<tr>
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<td></td>
<td>418.5330</td>
<td>4426.5630</td>
<td>11054.5890</td>
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</tbody>
</table>
Table A-14. Data of Concentration on Reactor with 100-pin for Different CO₂ to H₂O Ratio (Glow Regime, Voltage on Reactor = 0.814kV, Current = 0.42mA, Flow Rate of CO₂ = 50 sccm)

<table>
<thead>
<tr>
<th>CO₂ to H₂O Molar Ratio</th>
<th>Flow Rate of H₂O (ml/min)</th>
<th>Concentration of CO₂ (µmol/ml)</th>
<th>Concentration of H₂O (µmol/ml)</th>
<th>Concentration of O₂ (µmol/ml)</th>
<th>Concentration of CO (µmol/ml)</th>
<th>Concentration of CH₄ (µmol/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank (1:2)</td>
<td>0.081</td>
<td>20.649</td>
<td>41.912</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>0.081</td>
<td>19.798</td>
<td>41.443</td>
<td>0.806</td>
<td>0.560</td>
<td>0.280</td>
</tr>
<tr>
<td></td>
<td>0.081</td>
<td>19.773</td>
<td>41.441</td>
<td>0.806</td>
<td>0.584</td>
<td>0.292</td>
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<tr>
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<td>0.027</td>
<td>22.101</td>
<td>15.681</td>
<td>0.929</td>
<td>0.592</td>
<td>0.301</td>
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<tr>
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<td>0.027</td>
<td>21.204</td>
<td>15.137</td>
<td>0.930</td>
<td>0.593</td>
<td>0.301</td>
</tr>
<tr>
<td></td>
<td>0.027</td>
<td>21.202</td>
<td>15.141</td>
<td>0.931</td>
<td>0.595</td>
<td>0.302</td>
</tr>
<tr>
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<td>0.020</td>
<td>20.145</td>
<td>10.011</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>19.348</td>
<td>9.477</td>
<td>0.803</td>
<td>0.531</td>
<td>0.266</td>
</tr>
<tr>
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<td>0.020</td>
<td>19.352</td>
<td>9.481</td>
<td>0.802</td>
<td>0.532</td>
<td>0.264</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
<td>19.350</td>
<td>9.479</td>
<td>0.804</td>
<td>0.531</td>
<td>0.265</td>
</tr>
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<td>Blank (CO₂ only)</td>
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<td>21.766</td>
<td></td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
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<tr>
<td>CO₂ only</td>
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<td>0.443</td>
<td>0.882</td>
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<td>0.883</td>
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<td>20.927</td>
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<td>0.443</td>
<td>0.884</td>
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</table>
### Table A-15. Calculated Data on Reactor with 100-pin for Different CO\textsubscript{2} to H\textsubscript{2}O Ratio (Glow Regime, Voltage on Reactor = 0.814kV, Current = 0.42mA, Flow Rate of CO\textsubscript{2} = 50 sccm)

<table>
<thead>
<tr>
<th>CO\textsubscript{2} to H\textsubscript{2}O Molar Ratio</th>
<th>Flow Rate of H\textsubscript{2}O (sccm)</th>
<th>Conversion of CO\textsubscript{2} in Whole Reactor (%)</th>
<th>Conversion of CO\textsubscript{2} in Active Volume (%)</th>
<th>Energy Efficiency (%)</th>
<th>Reactor Efficiency (%)</th>
<th>Carbon Balance (\textmu mol/ml)</th>
<th>Hydrogen Balance (\textmu mol/ml)</th>
<th>Oxygen Balance (\textmu mol/ml)</th>
<th>Selectivity CH\textsubscript{4}/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank (1:2)</td>
<td>0.081</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.649</td>
<td>83.824</td>
<td>83.211</td>
<td>0.499</td>
</tr>
<tr>
<td>1:2</td>
<td>0.081</td>
<td>4.12</td>
<td>34.63</td>
<td>89.74</td>
<td>10.68</td>
<td>20.358</td>
<td>84.004</td>
<td>83.212</td>
<td>0.500</td>
</tr>
<tr>
<td></td>
<td>0.081</td>
<td>4.24</td>
<td>35.65</td>
<td>91.41</td>
<td>10.88</td>
<td>20.357</td>
<td>84.049</td>
<td>83.184</td>
<td>0.500</td>
</tr>
<tr>
<td></td>
<td>0.081</td>
<td>4.14</td>
<td>34.79</td>
<td>89.71</td>
<td>10.68</td>
<td>20.362</td>
<td>84.026</td>
<td>83.214</td>
<td>0.500</td>
</tr>
<tr>
<td>Blank (3:2)</td>
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<td></td>
<td></td>
<td></td>
<td>22.101</td>
<td>31.363</td>
<td>59.884</td>
<td>0.508</td>
</tr>
<tr>
<td>3:2</td>
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<td>34.10</td>
<td>97.27</td>
<td>11.57</td>
<td>21.796</td>
<td>31.477</td>
<td>59.996</td>
<td>0.509</td>
</tr>
<tr>
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<td>31.468</td>
<td>59.990</td>
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<tr>
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<td>4.07</td>
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<td>21.797</td>
<td>31.491</td>
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<tr>
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<td>50.302</td>
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<td>33.25</td>
<td>89.24</td>
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<td>19.884</td>
<td>20.019</td>
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<td>20.018</td>
<td>50.317</td>
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<tr>
<td>Blank (CO\textsubscript{2} only)</td>
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<td></td>
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<td></td>
<td>21.766</td>
<td>43.533</td>
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<td></td>
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<tr>
<td>CO\textsubscript{2} only</td>
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<td>21.809</td>
<td>43.623</td>
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<tr>
<td></td>
<td>3.86</td>
<td>32.42</td>
<td>57.17</td>
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<td>21.811</td>
<td>43.623</td>
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<td></td>
</tr>
</tbody>
</table>
B. Summary of Calibration Data Analytical

Two analytical sample gases (Sample 1: 1% O\textsubscript{2}, CO, CH\textsubscript{4} and CO\textsubscript{2} in N\textsubscript{2}; Sample 2: 4% O\textsubscript{2}, 7% CO, 4.5% CH\textsubscript{4} and 15% CO\textsubscript{2} in N\textsubscript{2}, v/v) and ultra-pure CO\textsubscript{2} gas (99.8% v/v) were used for calibrate O\textsubscript{2}, CO, CH\textsubscript{4} and CO\textsubscript{2}. Since at high concentration points, CO\textsubscript{2} can saturate the helium ionization detector (HID), the calibration curve of CO\textsubscript{2} was measured using thermal conductivity detector (TCD), while the others are still using HID for higher accuracy.

**Table B-1. Calculation of Injection Moles of O\textsubscript{2}, CO, CH\textsubscript{4} and CO\textsubscript{2}**

<table>
<thead>
<tr>
<th>Species</th>
<th>Percentage (%)</th>
<th>Volume of Sample Loop (ml)</th>
<th>Injection Volume (ml)</th>
<th>Density (g/ml)</th>
<th>Molar Mass (g/mol)</th>
<th>Injection Mole (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{2}</td>
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<td>0.0010</td>
<td>1.331×10\textsuperscript{-3}</td>
<td>3.2</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>21.00</td>
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<td>0.0210</td>
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<td>27.95</td>
<td>0.873</td>
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<tr>
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<td>1.165×10\textsuperscript{-3}</td>
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</tr>
<tr>
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<tr>
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<tr>
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<td>1.00</td>
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<td>0.0100</td>
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<td>11.65</td>
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</tr>
<tr>
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<td>700</td>
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<td>0.0175</td>
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<tr>
<td>CH\textsubscript{4}</td>
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<td>0.10</td>
<td>0.0010</td>
<td>6.680×10\textsuperscript{-4}</td>
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<tr>
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<tr>
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<td>0.0100</td>
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<tr>
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<td>0.0010</td>
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<tr>
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<td>4.95</td>
<td>0.113</td>
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<tr>
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<tr>
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<tr>
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<tr>
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<td>0.0998</td>
<td></td>
<td>197.60</td>
<td>4.491</td>
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</table>
For the calibration of water vapor, five aqueous solutions (Lithium Chloride, Potassium Acetate, Potassium Carbonate, Sodium Bromide and Sodium Chloride) with known concentration of water \(^77\) were prepared and injected at 100˚C.

### Table B-2. Calculation of Injection Moles of H\(_2\)O

<table>
<thead>
<tr>
<th>Aqueous Solution</th>
<th>Humidity (%)</th>
<th>Saturated Vapor Density (g/m(^3))</th>
<th>Actual Vapor Density (g/m(^3))</th>
<th>Molecular Mass (g/mol)</th>
<th>Volume of Sample Loop (ml)</th>
<th>Injection Mole (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium Chloride (LiCl)</td>
<td>10.5</td>
<td></td>
<td>2.417</td>
<td></td>
<td></td>
<td>13.425</td>
</tr>
<tr>
<td>Potassium Acetate (CH(_3)COOK)</td>
<td>21.6</td>
<td></td>
<td>4.971</td>
<td></td>
<td></td>
<td>27.618</td>
</tr>
<tr>
<td>Potassium Carbonate (K(_2)CO(_3))</td>
<td>43.2</td>
<td>23.015</td>
<td>9.942</td>
<td>18</td>
<td>1.00</td>
<td>55.236</td>
</tr>
<tr>
<td>Sodium Bromide (NaBr)</td>
<td>51.4</td>
<td></td>
<td>11.830</td>
<td></td>
<td></td>
<td>65.721</td>
</tr>
<tr>
<td>Sodium Chloride (NaCl)</td>
<td>76.3</td>
<td></td>
<td>17.560</td>
<td></td>
<td></td>
<td>97.558</td>
</tr>
</tbody>
</table>
B-1. Relative uncertainty

The procedure of calculating the relative uncertainty is shown below:

(1) Calculate the average

\[ \overline{A} = \frac{A_1 + A_2 + \cdots + A_m}{m} \]  
(Eq. B-1)

(2) Calculate the standard deviation

\[ \sigma = \sqrt{\frac{\sum_{i=1}^{N} (A_i - \overline{A})^2}{m-1}} \]  
(Eq. B-2)

(3) Calculate the standard error (or standard deviation of the mean)

\[ \sigma_m = \frac{\sigma}{\sqrt{m}} \]  
(Eq. B-3)

(4) Determine the relative uncertainty

Relative uncertainty \( = \frac{\sigma_m}{A} \)  
(Eq. B-4)

The results are shown below in Table B-2:
Table B-3. Relative Uncertainty of Peak Areas of Products and Reactants

<table>
<thead>
<tr>
<th>Species</th>
<th>Injection Mole (μmol)</th>
<th>Peak Area (mV·sec)</th>
<th>Average</th>
<th>Standard Deviation</th>
<th>Relative Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O₂</strong></td>
<td>0.043</td>
<td>2269.4779</td>
<td>2572.9385</td>
<td>2472.1520</td>
<td>2438.1895</td>
</tr>
<tr>
<td></td>
<td>0.107</td>
<td>5020.1636</td>
<td>5571.5002</td>
<td>5549.3808</td>
<td>5380.3482</td>
</tr>
<tr>
<td></td>
<td>0.166</td>
<td>11053.8796</td>
<td>10843.9324</td>
<td>11048.4976</td>
<td>10982.1032</td>
</tr>
<tr>
<td></td>
<td>0.416</td>
<td>18180.6330</td>
<td>18537.9073</td>
<td>18763.5508</td>
<td>18494.0304</td>
</tr>
<tr>
<td></td>
<td>0.873</td>
<td>34204.0258</td>
<td>34772.0111</td>
<td>35885.5808</td>
<td>34953.8726</td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td>0.042</td>
<td>3462.6804</td>
<td>3252.6384</td>
<td>3226.1430</td>
<td>3313.8206</td>
</tr>
<tr>
<td></td>
<td>0.104</td>
<td>5761.8702</td>
<td>6154.7710</td>
<td>6176.8116</td>
<td>6031.1509</td>
</tr>
<tr>
<td></td>
<td>0.291</td>
<td>20659.2512</td>
<td>20889.1232</td>
<td>20989.0973</td>
<td>20845.8239</td>
</tr>
<tr>
<td></td>
<td>0.416</td>
<td>22536.3198</td>
<td>23521.8160</td>
<td>23693.9116</td>
<td>23250.6787</td>
</tr>
<tr>
<td></td>
<td>0.728</td>
<td>36273.6932</td>
<td>36627.3748</td>
<td>36791.1388</td>
<td>36564.0689</td>
</tr>
<tr>
<td><strong>CH₄</strong></td>
<td>0.042</td>
<td>8010.4138</td>
<td>7908.3592</td>
<td>7749.1350</td>
<td>7919.6360</td>
</tr>
<tr>
<td></td>
<td>0.104</td>
<td>14374.4286</td>
<td>15037.5540</td>
<td>14242.8636</td>
<td>14551.6154</td>
</tr>
<tr>
<td></td>
<td>0.188</td>
<td>29837.6782</td>
<td>31028.1185</td>
<td>31097.0548</td>
<td>30654.2838</td>
</tr>
<tr>
<td></td>
<td>0.418</td>
<td>47087.9762</td>
<td>49491.2204</td>
<td>49575.5588</td>
<td>48718.2518</td>
</tr>
<tr>
<td></td>
<td>0.470</td>
<td>50673.0514</td>
<td>51102.0996</td>
<td>51327.7249</td>
<td>51034.2920</td>
</tr>
<tr>
<td><strong>CO₂</strong></td>
<td>0.045</td>
<td>3.5638</td>
<td>3.2011</td>
<td>3.4908</td>
<td>3.4186</td>
</tr>
<tr>
<td></td>
<td>0.113</td>
<td>8.8266</td>
<td>8.9724</td>
<td>9.4281</td>
<td>9.0757</td>
</tr>
<tr>
<td></td>
<td>0.450</td>
<td>37.9670</td>
<td>38.8594</td>
<td>37.4756</td>
<td>38.1007</td>
</tr>
<tr>
<td></td>
<td>0.675</td>
<td>50.5214</td>
<td>54.0154</td>
<td>55.1837</td>
<td>53.2402</td>
</tr>
<tr>
<td></td>
<td>1.688</td>
<td>127.3712</td>
<td>128.2948</td>
<td>129.7458</td>
<td>128.4706</td>
</tr>
<tr>
<td></td>
<td>4.491</td>
<td>353.6928</td>
<td>351.8537</td>
<td>354.5578</td>
<td>353.3681</td>
</tr>
<tr>
<td><strong>H₂O</strong></td>
<td>13.425</td>
<td>0.1144</td>
<td>0.1147</td>
<td>0.1150</td>
<td>0.1147</td>
</tr>
<tr>
<td></td>
<td>27.618</td>
<td>0.3574</td>
<td>0.3572</td>
<td>0.3573</td>
<td>0.3573</td>
</tr>
<tr>
<td></td>
<td>55.236</td>
<td>3.2548</td>
<td>3.2536</td>
<td>3.2527</td>
<td>3.2537</td>
</tr>
<tr>
<td></td>
<td>65.721</td>
<td>7.5375</td>
<td>7.5278</td>
<td>7.5176</td>
<td>7.5276</td>
</tr>
<tr>
<td></td>
<td>97.558</td>
<td>96.2167</td>
<td>96.1169</td>
<td>96.0166</td>
<td>96.1167</td>
</tr>
</tbody>
</table>
B-2. Dixon’s Test

The procedure of the Dixon’s test (or Q-test) is shown as below:

1. Calculate the range

\[ w = A_{\text{max}} - A_{\text{min}} \]  
(Eq. B-5)

2. Calculate the gap

\[ \text{gap} = \left| A_{\text{questionable}} - A_{\text{neighbor}} \right| \]  
(Eq. B-6)

3. Calculate the Q value

\[ Q = \frac{\text{gap}}{w} \]  
(Eq. B-7)

4. Look up the Q value in the Dixon test Table (Table B-4)\(^7\) according to the measurement number. We choose confidence interval as 99%. If \( Q > Q_{\text{table}} \) (In this case, \( Q_{\text{table}} = 0.988 \)), the datum is an outlier, so we need to reject it; if \( Q < Q_{\text{table}} \), the datum is not an outlier.

Table B-4. Critical Values for the Dixon’s Test of Outliers

<table>
<thead>
<tr>
<th>Test Statistic</th>
<th>Level of significance α</th>
<th>0.30</th>
<th>0.20</th>
<th>0.10</th>
<th>0.05</th>
<th>0.02</th>
<th>0.01</th>
<th>0.005</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( r_{10} = \frac{x_2 - x_1}{x_n - x_1} )</td>
<td>3</td>
<td>0.684</td>
<td>0.781</td>
<td>0.886</td>
<td>0.941</td>
<td>0.976</td>
<td>0.988</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.471</td>
<td>0.560</td>
<td>0.679</td>
<td>0.765</td>
<td>0.846</td>
<td>0.889</td>
<td>0.926</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.373</td>
<td>0.451</td>
<td>0.557</td>
<td>0.642</td>
<td>0.729</td>
<td>0.780</td>
<td>0.821</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.318</td>
<td>0.366</td>
<td>0.482</td>
<td>0.560</td>
<td>0.644</td>
<td>0.698</td>
<td>0.740</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.281</td>
<td>0.344</td>
<td>0.434</td>
<td>0.507</td>
<td>0.596</td>
<td>0.637</td>
<td>0.680</td>
</tr>
</tbody>
</table>

The result of the Dixon’s test is shown below in Table B-4:
Table B-5. Results of the Dixon’s Test for Products and Reactants

<table>
<thead>
<tr>
<th>Species</th>
<th>Injection Mole (μmol)</th>
<th>Maximum</th>
<th>Minimum</th>
<th>Range</th>
<th>Questionable Value</th>
<th>Gap</th>
<th>Q Value</th>
<th>Outlier or not</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2</td>
<td>0.043</td>
<td>2572.9385</td>
<td>2269.4779</td>
<td>303.4606</td>
<td>2269.478</td>
<td>202.6741</td>
<td>0.668</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>0.107</td>
<td>5571.5002</td>
<td>5020.1636</td>
<td>551.3366</td>
<td>5020.164</td>
<td>529.2172</td>
<td>0.960</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>0.166</td>
<td>11053.8796</td>
<td>10843.9324</td>
<td>209.9472</td>
<td>10843.93</td>
<td>204.5652</td>
<td>0.974</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>0.416</td>
<td>18763.5508</td>
<td>18180.6330</td>
<td>582.9178</td>
<td>18180.63</td>
<td>357.2743</td>
<td>0.613</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>0.873</td>
<td>35885.5808</td>
<td>34204.0258</td>
<td>3585.58</td>
<td>3585.58</td>
<td>1113.5697</td>
<td>0.662</td>
<td>No</td>
</tr>
<tr>
<td>CO</td>
<td>0.042</td>
<td>3462.6804</td>
<td>3226.1430</td>
<td>236.5374</td>
<td>3462.68</td>
<td>210.0420</td>
<td>0.888</td>
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</tr>
<tr>
<td></td>
<td>0.104</td>
<td>6176.8116</td>
<td>5761.8702</td>
<td>414.9414</td>
<td>5761.87</td>
<td>392.9008</td>
<td>0.947</td>
<td>No</td>
</tr>
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<td>20659.2512</td>
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<td>20659.25</td>
<td>229.8720</td>
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<td>No</td>
</tr>
<tr>
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<td>22536.3200</td>
<td>1157.5800</td>
<td>22536.32</td>
<td>985.4960</td>
<td>0.851</td>
<td>No</td>
</tr>
<tr>
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<td>0.728</td>
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<td>36273.6932</td>
<td>517.4456</td>
<td>36273.69</td>
<td>353.6816</td>
<td>0.684</td>
<td>No</td>
</tr>
<tr>
<td>CH4</td>
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<td>8101.4138</td>
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<td>352.2788</td>
<td>8101.414</td>
<td>193.0546</td>
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<td>No</td>
</tr>
<tr>
<td></td>
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<td>15037.5540</td>
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<td>794.6904</td>
<td>15037.55</td>
<td>663.1254</td>
<td>0.834</td>
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</tr>
<tr>
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<td>29837.6782</td>
<td>1259.3766</td>
<td>29837.68</td>
<td>1190.4403</td>
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<td>No</td>
</tr>
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<td>0.418</td>
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<td>47087.9762</td>
<td>2487.5826</td>
<td>47087.98</td>
<td>2403.2442</td>
<td>0.966</td>
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</tr>
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<td>51327.7249</td>
<td>50673.0514</td>
<td>654.6735</td>
<td>50673.05</td>
<td>429.0482</td>
<td>0.655</td>
<td>No</td>
</tr>
<tr>
<td>CO2</td>
<td>0.045</td>
<td>3.5638</td>
<td>3.2011</td>
<td>0.3627</td>
<td>3.2011</td>
<td>0.2897</td>
<td>0.799</td>
<td>No</td>
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<tr>
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<td>0.113</td>
<td>9.4281</td>
<td>8.8266</td>
<td>0.6015</td>
<td>9.4281</td>
<td>0.4557</td>
<td>0.758</td>
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<td>1.3838</td>
<td>38.8594</td>
<td>0.8924</td>
<td>0.645</td>
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</tr>
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<td>0.675</td>
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<td>50.5214</td>
<td>4.6623</td>
<td>50.5214</td>
<td>3.4940</td>
<td>0.749</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>1.688</td>
<td>129.7458</td>
<td>127.3712</td>
<td>2.3746</td>
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<td>H2O</td>
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<td>0.1144</td>
<td>0.0006</td>
<td>0.1144</td>
<td>0.0003</td>
<td>0.500</td>
<td>No</td>
</tr>
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<td>27.618</td>
<td>0.3574</td>
<td>0.3572</td>
<td>0.0002</td>
<td>0.3572</td>
<td>0.0001</td>
<td>0.500</td>
<td>No</td>
</tr>
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<td>55.236</td>
<td>3.2548</td>
<td>3.2527</td>
<td>0.0021</td>
<td>3.2548</td>
<td>0.0012</td>
<td>0.571</td>
<td>No</td>
</tr>
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<td></td>
<td>65.721</td>
<td>7.5375</td>
<td>7.5176</td>
<td>0.0199</td>
<td>7.5176</td>
<td>0.0102</td>
<td>0.513</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>97.558</td>
<td>96.2167</td>
<td>96.0166</td>
<td>0.2001</td>
<td>96.0166</td>
<td>0.1003</td>
<td>0.501</td>
<td>No</td>
</tr>
</tbody>
</table>
B-3. Linear Regression Analysis

For linear line $y = mx + b$, 

$$
m = \frac{\sum_{i=1}^{n} x_i y_i - \left( \sum_{i=1}^{n} x_i \right) \left( \sum_{i=1}^{n} y_i \right)}{n \sum_{i=1}^{n} x_i^2 - \left( \sum_{i=1}^{n} x_i \right)^2} \tag{Eq. B-8}
$$

$$
\begin{align*}
b &= \bar{y} - m\bar{x} \tag{Eq. B-9}
\end{align*}
$$

If this fit line is forced to pass through origin,

$$
m = \frac{\sum_{i=1}^{n} x_i y_i}{\sum_{i=1}^{n} x_i^2} \tag{Eq. B-10}
$$

For exponential line $y = Ae^{Bx}$ (ln y = ln A + Bx),

$$
B = m = \frac{\sum_{i=1}^{n} x_i \ln y_i - \left( \sum_{i=1}^{n} x_i \right) \left( \sum_{i=1}^{n} \ln y_i \right)}{n \sum_{i=1}^{n} x_i^2 - \left( \sum_{i=1}^{n} x_i \right)^2} \tag{Eq. B-11}
$$

$$
\begin{align*}
b &= \frac{\sum_{i=1}^{n} \ln y_i \sum_{i=1}^{n} x_i^2 - \left( \sum_{i=1}^{n} x_i \right) \left( \sum_{i=1}^{n} \ln y_i \right)}{n \sum_{i=1}^{n} x_i^2 - \left( \sum_{i=1}^{n} x_i \right)^2} \tag{Eq. B-12}
\end{align*}
$$

$$
A = e^b \tag{Eq. B-13}
$$

Sum of squares for the residuals

$$
SS_{res} = \sum_{i=1}^{n} \left[ y_i - \bar{y}_i \right]^2 \tag{Eq. B-14}
$$

Overall variability of the data
\[ SS_{total} = \sum_{i=1}^{n} y_i^2 - \frac{1}{n} \left( \sum_{i=1}^{n} y_i \right)^2 \]  
(Eq. B-15)

The coefficient of determination uses the relative sizes of the variability explained by the regression model and the total variability to measure the overall adequacy of the model.

\[ R^2 = 1 - \frac{SS_{res}}{SS_{total}} \quad (0 \leq R^2 \leq 1) \]  
(Eq. B-16)

For models that fit the data well, \( R^2 \) is near 1. Models that poorly fit the data have \( R^2 \) near 0.

The result of recalculating the best fit line is shown below in Table B-6, B-7 and B-8:

**Table B-6. Linear Regression Analysis Results for O\(_2\), CO, CH\(_4\) and CO\(_2\)**

<table>
<thead>
<tr>
<th>Species</th>
<th>( \sum x_i )</th>
<th>( \bar{x} )</th>
<th>( \sum y_i )</th>
<th>( \bar{y} )</th>
<th>( \sum x_i y_i )</th>
<th>( \sum x_i^2 )</th>
<th>( m )</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>4.82\times10^{-6}</td>
<td>3.21\times10^{-7}</td>
<td>216745.63</td>
<td>14449.71</td>
<td>0.12</td>
<td>2.93\times10^{-12}</td>
<td>4.17\times10^{10}</td>
<td>0</td>
</tr>
<tr>
<td>CO</td>
<td>4.74\times10^{-6}</td>
<td>3.16\times10^{-7}</td>
<td>270016.64</td>
<td>18001.11</td>
<td>0.13</td>
<td>2.40\times10^{-12}</td>
<td>5.39\times10^{10}</td>
<td>0</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>3.67\times10^{-6}</td>
<td>2.44\times10^{-7}</td>
<td>458634.24</td>
<td>30575.62</td>
<td>0.16</td>
<td>1.33\times10^{-12}</td>
<td>1.17\times10^{11}</td>
<td>0</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>2.24\times10^{-5}</td>
<td>1.24\times10^{-6}</td>
<td>1757.02</td>
<td>97.61</td>
<td>0.57\times10^{-3}</td>
<td>7.11\times10^{-11}</td>
<td>7.84\times10^{7}</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table B-7. Linear Regression Analysis Result for H\(_2\)O**

<table>
<thead>
<tr>
<th>Species</th>
<th>( \sum x_i )</th>
<th>( \bar{x} )</th>
<th>( \sum \ln y_i )</th>
<th>( \bar{y} )</th>
<th>( \sum x_i \ln y_i )</th>
<th>( \sum x_i^2 )</th>
<th>( m )</th>
<th>( b )</th>
<th>( A )</th>
<th>( B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>7.79\times10^{-5}</td>
<td>5.19\times10^{-6}</td>
<td>13.71</td>
<td>21.47</td>
<td>1.76\times10^{-4}</td>
<td>5.35\times10^{-10}</td>
<td>8\times10^{5}</td>
<td>-3.24</td>
<td>0.039</td>
<td>2</td>
</tr>
</tbody>
</table>
### Table B-8. Coefficient of Determination for O₂, CO, CH₄, CO₂ and H₂O

<table>
<thead>
<tr>
<th>Species</th>
<th>Sum of Squares for Residuals $SS_{res}$</th>
<th>Overall Variability in the Data $SS_{total}$</th>
<th>Coefficient of Determination $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>6.54×10⁷</td>
<td>2.03×10⁹</td>
<td>0.968</td>
</tr>
<tr>
<td>CO</td>
<td>1.08×10⁸</td>
<td>2.22×10⁹</td>
<td>0.951</td>
</tr>
<tr>
<td>CH₄</td>
<td>3.22×10⁸</td>
<td>4.56×10⁹</td>
<td>0.929</td>
</tr>
<tr>
<td>CO₂</td>
<td>9.38×10¹</td>
<td>2.31×10⁵</td>
<td>1.000</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.02×10⁻²</td>
<td>2.10×10⁴</td>
<td>1.000</td>
</tr>
</tbody>
</table>

**Figure 104. Calibration Curve of Oxygen on Gas Chromatography (Helium Ionization Detector)**
Figure 105. Calibration Curve of Carbon Monoxide on Gas Chromatography (Helium Ionization Detector)

Figure 106. Calibration Curve of Methane on Gas Chromatography (Helium Ionization Detector)
Figure 107. Calibration Curve of Carbon Dioxide on Gas Chromatography (Thermal Conductivity Detector)

Figure 108. Calibration Curve of Water on Gas Chromatography (Helium Ionization Detector)
C. Design Calculations of Power for Evaporator

Before the manufacture of evaporator, the power of the heating source (heating tapes in this study) needs to be calculated so it can satisfy the requirements of the evaporator. Two heating powers (startup power and operating power) are calculated and compared to determine the power of heating tapes used in the system.

1. Startup power

\[ P_1 = P_{\text{fluid}} + P_{\text{tube}} = n_{\text{fluid}}C_{P,\text{fluid}}\Delta T + m_{\text{tube}}C_{P,\text{tube}}\Delta T \]

(Eq. C-1)

where \( n_{\text{fluid}} \) is mole of the fluid, unit: mol;

\( C_{P,\text{fluid}} \) is heat capacity of fluid, unit: kJ/(mol·°C);

\( C_{P,\text{tube}} \) is heat capacity of stainless steel tube, unit: kJ/(kg·°C), \( C_{P,\text{tube}} \approx 0.4184\) kJ/(kg·°C);

\( \Delta T \) is the temperature change, unit: °C;

\( m_{\text{tube}} \) is the mass of the tube, unit: kg;

\( t \) is the heating time during \( \Delta T \), unit: min, \( t = 20 \) min.

The heat capacity of the fluid can be calculated using the equation below:

\[ C_p = a + bT + cT^2 + dT^3 \]

(Eq. C-2)

From the literature,\(^7^9\) the value of \( a, b, c \) and \( d \) for \( CO_2 \) and water (liquid and vapor) can be found.
### Table C-1. Constants of Heat Capacities

<table>
<thead>
<tr>
<th>Compounds</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3.61×10⁻²</td>
<td>4.23×10⁻⁵</td>
<td>-2.887×10⁻⁸</td>
<td>7.464×10⁻¹²</td>
</tr>
<tr>
<td>H₂O (l)</td>
<td>7.54×10⁻²</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O (g)</td>
<td>3.35×10⁻²</td>
<td>6.88×10⁻⁶</td>
<td>7.604×10⁻⁹</td>
<td>-3.593×10⁻¹²</td>
</tr>
</tbody>
</table>

Since the fluid flow through the evaporator is a mixture of CO₂ and water, heat capacity of mixture is calculated:

\[
C_{P,\text{fluid}} = x_1 \left( a_1 + b_1 T + c_1 T^2 + d_1 T^3 \right) + x_2 \left( a_2 + b_2 T + c_2 T^2 + d_2 T^3 \right)
\]  
(Eq. C-3)

where \( x_1 \) and \( x_2 \) are respectively the molar fraction of CO₂ and water in the fluid (\( x_1 = 0.33, x_2 = 0.67 \)).

Since the heating process is from 25°C to 110°C and water can be transferred from liquid phase to gas phase, the process needs to be divided into three parts for calculation: from 25°C to 100°C, water phase change, and from 100°C to 110°C. Therefore,

\[
\Delta H_{\text{fluid}} = \left( n_{CO_2} + n_{H_2O} \right) \int_{T_1}^{T_2} C_{P,\text{fluid}}(T) \,dT + n_{H_2O} \Delta H_v + \left( n_{CO_2} + n_{H_2O} \right) \int_{T_2}^{T} C'_{P,\text{fluid}}(T) \,dT
\]  
(Eq. C-4)

where \( n_{CO_2} \) and \( n_{H_2O} \) are respectively the mole of CO₂ and water, unit: mol;

\( T_1, T_2 \) and \( T \) are temperatures, unit: °C, \( T_1 = 25°C, T_2 = 100°C, T = 110°C \);

\( C_{P,\text{fluid}} \) and \( C'_{P,\text{fluid}} \) are respectively the heat capacity of mixture CO₂ and liquid water and mixture CO₂ and water vapor, unit: kJ/(mol·°C);

\( \Delta H_v \) is the heat of vaporization of water at 100°C, unit: kJ/mol,

\[
\Delta H_v = 40.656 \text{kJ/mole}.
\]

The evaporator is built on a stainless tube. The dimensions of the tube are: length = 0.24m, outer diameter = 0.003175m (1/8 inches), and inner diameter = 0.002032m (0.08 inches). The volume of the channel and tube are:
\[ V_{\text{fluid}} = \pi \left( \frac{d}{2} \right)^2 l = \pi \left( \frac{0.002032m}{2} \right)^2 \times 0.24m = 7.78 \times 10^{-7} \text{ m}^3 = 0.778 ml \]  

(Eq. C-5)

\[ V_{\text{tube}} = \pi l \left[ \left( \frac{d_x}{2} \right)^2 - \left( \frac{d_y}{2} \right)^2 \right] = \pi \times 0.24m \times \left[ \left( \frac{0.003175m}{2} \right)^2 - \left( \frac{0.002032m}{2} \right)^2 \right] 
\]

= \(1.12 \times 10^{-6} \text{ m}^3 = 1.12 ml\)  

(Eq. C-6)

The moles of CO\(_2\) and water can be calculated: \(n_{CO_2} = \frac{\rho_{CO_2} x_{C} V_{fluid}}{M_{CO_2}}\) and \(n_{H_2O} = \frac{\rho_{H_2O} x_{H} V_{fluid}}{M_{H_2O}}\).

### Table C-2. Selected Physical Property Data of CO\(_2\) and Water

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Molar Fraction (%)</th>
<th>Density (g/ml)</th>
<th>Molar Mass (g/mol)</th>
<th>Mole (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>0.33</td>
<td>1.98\times10^{-3}</td>
<td>44</td>
<td>1.15\times10^{-5}</td>
</tr>
<tr>
<td>H(_2O)</td>
<td>0.67</td>
<td>1.00</td>
<td>18</td>
<td>0.029</td>
</tr>
</tbody>
</table>

Therefore, \(\Delta H_{\text{fluid}} = 1.33 kJ\)

\[ m_{\text{tube}} = \rho_{\text{tube}} V_{\text{tube}} = 7.8 \text{ g/ml} \times 1.12 \text{ ml} = 8.746 \text{ g} = 8.746 \times 10^{-3} \text{ kg} \]  

(Eq. C-7)

\[ P_1 = \frac{\Delta H_{\text{fluid}} + m_{\text{tube}} C_{\text{P,tube}} \Delta T}{t} \]

\[ = \frac{1.33 kJ + 8.746 \times 10^{-3} \text{ kg} \times 0.4184 \text{ kJ/(kg \cdot C)} \times (110C - 25C)}{20 \text{ min} \times 60 \text{ sec/min}} = 1.36W \]  

(Eq. C-8)

Take 20% power margin, \(P_1 = 1.2 \times 1.36W = 1.64W\)

2. Operating power

\[ P_2 = P_{\text{fluid}}' = \dot{n}_m C_{\text{P,fluid}} \Delta T \]  

(Eq. C-9)
Similar to the calculation above, the process also needs to be divided into three parts for calculation: from 25°C to 100°C, water phase change, and from 100°C to 110°C.

\[
P_2 = \Delta H_{\text{fluid}} = \left(\dot{n}_{\text{CO}_2} + \dot{n}_{\text{H}_2\text{O}}\right) \int_{T_1}^{T_2} C_{p,\text{fluid}}(T) \, dT + n_{\text{H}_2\text{O}} \Delta H_v + \left(\dot{n}_{\text{CO}_2} + \dot{n}_{\text{H}_2\text{O}}\right) \int_{T_2}^{T_3} C'_{p,\text{fluid}}(T) \, dT
\]

(Eq. C-10)

\[
\dot{n}_{\text{CO}_2} = \frac{\rho_{\text{CO}_2} \dot{V}_{\text{CO}_2}}{M_{\text{CO}_2}} = \frac{1.98 \times 10^{-3} \, \text{g/ml} \times 100 \, \text{ml/min}}{44 \, \text{g/mol}} = 7.5 \times 10^{-5} \, \text{mol/sec}
\]

(Eq. C-11)

\[
\dot{n}_{\text{H}_2\text{O}} = 2\dot{n}_{\text{CO}_2} = 1.5 \times 10^{-4} \, \text{mol/sec}
\]

(Eq. C-12)

\[
P_2 = 7.25 \times 10^{-3} \, \text{kJ/sec} = 7.25 \, \text{W}
\]

(Eq. C-13)

Since \(P_1 < P_2\), power of the heat tapes has to be at least 8W.
D. Parameters for Energy Analysis

Table D-1. Enthalpy of Formation for Chemical Compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Enthalpy of Formation (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (g)</td>
<td>-393.52</td>
</tr>
<tr>
<td>H₂O (g)</td>
<td>-241.83</td>
</tr>
<tr>
<td>CO (g)</td>
<td>-110.53</td>
</tr>
<tr>
<td>O₂ (g)</td>
<td>0</td>
</tr>
<tr>
<td>CH₄ (g)</td>
<td>-74.6</td>
</tr>
</tbody>
</table>

Table D-2. Shomate Constants for Chemical Compounds

<table>
<thead>
<tr>
<th>Component</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (g)</td>
<td>24.99735</td>
<td>55.18696</td>
<td>-33.69137</td>
<td>7.948387</td>
<td>-0.136638</td>
<td>-403.6075</td>
<td>228.2431</td>
<td>-393.5224</td>
</tr>
<tr>
<td>H₂O (g)</td>
<td>30.09200</td>
<td>6.832514</td>
<td>6.793435</td>
<td>-2.534480</td>
<td>0.082139</td>
<td>-250.8810</td>
<td>223.3967</td>
<td>-241.8264</td>
</tr>
<tr>
<td>CO (g)</td>
<td>25.56759</td>
<td>6.096130</td>
<td>4.054656</td>
<td>-2.671301</td>
<td>0.131021</td>
<td>-118.0089</td>
<td>227.3665</td>
<td>-110.5271</td>
</tr>
<tr>
<td>O₂ (g)</td>
<td>31.32234</td>
<td>-20.23531</td>
<td>57.86644</td>
<td>-36.50624</td>
<td>-0.007374</td>
<td>-8.903471</td>
<td>246.7945</td>
<td>0.0</td>
</tr>
<tr>
<td>CH₄ (g)</td>
<td>-0.703029</td>
<td>108.4773</td>
<td>-42.52157</td>
<td>5.862788</td>
<td>0.678565</td>
<td>-76.84376</td>
<td>158.7163</td>
<td>-74.87310</td>
</tr>
</tbody>
</table>
E. Calculation of Reynolds Number for Reactor Design

For a parallel plate system, Reynolds number can be calculated using the following equation:

\[ \text{Re} = \frac{dv \rho}{\mu} \]  

(Eq. D-1)

where \( d \) is the gap distance between two parallel plates, \( d = 110 \mu m = 1.1 \times 10^{-4} m \);

\( v \) is the average velocity of the fluid flow, \( m/sec \);

\( \rho \) is the density of the mixture, \( kg/m^3 \);

\( \mu \) is the viscosity of the mixture, \( Pa \cdot sec \).

1. Average velocity

The highest volumetric flow rate is 80 \( sccm \) and the width of the reaction channel is 7.6\( mm \), therefore the average velocity

\[ v = \frac{\dot{V}}{W \cdot d} = \frac{80 ml/min}{7.6 mm \times 1.1 \times 10^{-4} m} = 1.59 m/sec \]  

(Eq. D-2)

2. Density of the mixture

Assume total volume of gases is \( V \),

Since molar fraction of \( \text{CO}_2 \) and water vapor is 33\% and 67\%, the volumes for these two gases are \( 0.33V \) and \( 0.67V \) respectively.

\[ m_{\text{CO}_2} = M_{\text{CO}_2} \cdot n_{\text{CO}_2} = \frac{M_{\text{CO}_2} \cdot p \cdot V_{\text{CO}_2}}{RT} = \frac{44 g/mol \times p \times 0.33V}{RT} = 14.52 \frac{pV}{RT} [g] \]  

(Eq. D-3)

\[ m_{\text{H}_2\text{O}} = M_{\text{H}_2\text{O}} \cdot n_{\text{H}_2\text{O}} = \frac{M_{\text{H}_2\text{O}} \cdot p \cdot V_{\text{H}_2\text{O}}}{RT} = \frac{18 g/mol \times p \times 0.67V}{RT} = 12.06 \frac{pV}{RT} [g] \]  

(Eq. D-4)

\[ m_{\text{mixture}} = m_{\text{CO}_2} + m_{\text{H}_2\text{O}} = 25.58 \frac{pV}{RT} [g] \]  

(Eq. D-5)

Since pressure \( p = 101.325 kPa \), gas constant \( R = 8.314 J/(K \cdot mol) \), temperature \( T = 383 K \),
\[ m_{\text{mixture}} = 25.58 \frac{pV}{RT} = 25.58 \text{ g/mol} \times \frac{101.325 \text{kPa} \times V}{8.314 \text{ J/(K mol)} \times 383 \text{ K}} = 0.81V[\text{g}] \]  
\text{(Eq. D-6)}

\[ \rho = \frac{m_{\text{mixture}}}{V} = \frac{0.81V[\text{g}]}{V[\text{L}]} = 0.65 \text{ g/L} = 0.65 \text{ kg/m}^3 \]  
\text{(Eq. D-7)}

3. Viscosity of the mixture

Apply Chapman-Enskog equation to estimate viscosities of CO\textsubscript{2} and water vapor at 383K,

\[ \mu = 2.6693 \times 10^{-5} \sqrt{\frac{MT}{\sigma_{ik}^2 \Omega}} \]  
\text{(Eq. D-8)}

where \( \mu \) is gas viscosity, \( \text{Pa}\cdot\text{sec} \);

\( M \) is molecular mass, \( \text{g/mol} \);

\( T \) is temperature, \( T = 383 \text{K} \);

\( \sigma_{ik} \) is the collision diameter, \( \text{Å} \);

\( \Omega \) is the collision integral, \( K \), which is the function of reduced temperature \( k_B T/\varepsilon \),

where \( \varepsilon/k_B \) is the maximum energy of attraction divided by the Boltzmann constant.

From the literature \(^{80}\), the collision diameters and the maximum energies of attraction divided by the Boltzmann constant of CO\textsubscript{2} and H\textsubscript{2}O molecules can be found:

\[ \sigma_{ik, \text{CO}_2} = 4.00 \text{Å}, \sigma_{ik, \text{H}_2\text{O}} = 2.65 \text{Å}, \left( \frac{\varepsilon}{k_B} \right)_{\text{CO}_2} = 190.0K, \left( \frac{\varepsilon}{k_B} \right)_{\text{H}_2\text{O}} = 356K \]

The collision integrals of CO\textsubscript{2} and H\textsubscript{2}O molecules can be found according to the value of \( k_B T/\varepsilon \):

\[ \Omega_{\text{CO}_2} = 1.075K, \Omega_{\text{H}_2\text{O}} = 356K \]
\[ \mu_{\text{CO}_2} = 2.6693 \times 10^{-5} \sqrt{\frac{M_{\text{CO}_2} T}{\sigma_{\text{CO}_2}^2 \Omega_{\text{CO}_2}}} = 2.6693 \times 10^{-5} \times \frac{\sqrt{44 \text{ g/mol} \times 383K}}{(4.00 \text{ Å})^2 \times 1.075} \]  
\[ \text{(Eq. D-9)} \]
\[ = 2.01 \times 10^{-4} \text{P} = 2.01 \times 10^{-5} \text{Pa} \cdot \text{s} \]

\[ \mu_{\text{H}_2\text{O}} = 2.6693 \times 10^{-5} \sqrt{\frac{M_{\text{H}_2\text{O}} T}{\sigma_{\text{H}_2\text{O}}^2 \Omega_{\text{H}_2\text{O}}}} = 2.6693 \times 10^{-5} \times \frac{\sqrt{18 \text{ g/mol} \times 383K}}{(2.65 \text{ Å})^2 \times 1.406} \]  
\[ \text{(Eq. D-10)} \]
\[ = 2.24 \times 10^{-4} \text{P} = 2.24 \times 10^{-5} \text{Pa} \cdot \text{s} \]

\[ \mu = \frac{y_{\text{CO}_2} \mu_{\text{CO}_2} M_{\text{CO}_2} + y_{\text{H}_2\text{O}} \mu_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}}{y_{\text{CO}_2} M_{\text{CO}_2} + y_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}}} \]
\[ = \frac{0.33 \times 2.01 \times 10^{-5} \text{Pa} \cdot \text{s} \times 44 \text{ g/mol} + 0.67 \times 2.24 \times 10^{-5} \text{Pa} \cdot \text{s} \times 18 \text{ g/mol}}{0.33 \times 44 \text{ g/mol} + 0.67 \times 18 \text{ g/mol}} \]
\[ = 2.11 \times 10^{-5} \text{Pa} \cdot \text{s} \]  
\[ \text{(Eq. D-11)} \]

\[ \text{Re} = \frac{dv \rho}{\mu} = \frac{1.1 \times 10^{-4} \text{m} \times 1.59 \text{ m/sec} \times 0.65 \text{ kg/m}^3}{2.11 \times 10^{-5} \text{Pa} \cdot \text{s}} \approx 1.5 << 2000 \]  
\[ \text{(Eq. D-12)} \]

Therefore, the flow is laminar.
F. Calculation of the Binary Maxwell-Stefan Diffusivities

Binary Maxwell-Stefan diffusivities can be estimated from Chapman-Enskog kinetic theory

\[
D_{ik} = \frac{0.0018583 \sqrt{T^3 \left( \frac{1}{M_i} + \frac{1}{M_k} \right)}}{p\sigma_{ik}^2 \Omega}
\]  
(Eq. E-1)

where \( T \) is the temperature, \( T = 383K \);

\( M_i \) is the molecular weight of species \( i \), g/mol;

\( M_k \) is the molecular weight of species \( k \), g/mol;

\( p \) is the pressure, \( p = 1atm \);

\( \sigma_{ik} \) is binary collision diameter parameters, \( \hat{A}, \sigma_{ik} = \frac{\sigma_i + \sigma_k}{2} \);

\( \Omega \) is a temperature-dependent collision integral, which is a function of \( \varepsilon_{ik}/k_B \), \( \varepsilon_{ik} \) is the characteristic energy appearing in the Lennard-Jones potential for the binary pair, \( \varepsilon_{ik} = \sqrt{\varepsilon_i \varepsilon_k} \), \( k_B \) is the Boltzmann constant \((1.38 \times 10^{-23} \, J/K)\).

### Table F-1. Parameters for Chapman-Enskog Equation\(^{80}\)

<table>
<thead>
<tr>
<th></th>
<th>( M_i ) [g/mol]</th>
<th>( \sigma_i ) [Å]</th>
<th>( \varepsilon_{ik}/k_B ) [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>44</td>
<td>4.00</td>
<td>190</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>18</td>
<td>2.65</td>
<td>356</td>
</tr>
<tr>
<td>CO</td>
<td>28</td>
<td>3.59</td>
<td>110</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>16</td>
<td>3.80</td>
<td>144</td>
</tr>
<tr>
<td>O(_2)</td>
<td>32</td>
<td>3.54</td>
<td>88</td>
</tr>
</tbody>
</table>
Table F-2. Calculated Maxwell-Stefan Diffusivities (Unit: cm$^2$/sec)

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$</th>
<th>H$_2$O</th>
<th>CO</th>
<th>CH$_4$</th>
<th>O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.32</td>
<td></td>
<td>0.26</td>
<td>0.28</td>
<td>0.26</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
<td>0.32</td>
<td>0.43</td>
<td>0.44</td>
<td>0.51</td>
</tr>
<tr>
<td>CO</td>
<td>0.26</td>
<td>0.43</td>
<td></td>
<td>0.36</td>
<td>0.34</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.28</td>
<td>0.44</td>
<td>0.36</td>
<td></td>
<td>0.37</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.26</td>
<td>0.51</td>
<td>0.34</td>
<td>0.37</td>
<td></td>
</tr>
</tbody>
</table>
G. Procedure of Optimization of Numerical Model

1. Save COMSOL model as a m. file

In the COMSOL Multiphysics desktop, go to “File” → ”Compact History” to release the history of previous programming to reduce the computation time. Then, go to “File” → ”Save As”, choose “Model File for MATLAB (*.m)” under “Save as type:” and the directory, then click “OK”.

2. Modify the m. file to make it a function file for Matlab

Declare the m. file as a function with input and output variables, which would be the objective function. Then, modify this m. file by setting the target model parameters, extracting concentrations at certain position of the reactor by using the syntax `mphinterp` and calculating the average concentrations at the outlet surface using the syntax `mean`. Several such m. files need to be created, one for each condition (different voltage, current, flow rate, CO₂:H₂O molar ratio).

The code for the modified m. files (take one of them as example):

```matlab
function f = Concentration1(k)
    
    if k1<0,
        k1 = abs(k1);
    end
```
if k2<0,
k2 = abs(k2);
end
if k3<0,
k3 = abs(k3);
end
if k4<0,
k4 = abs(k4);
end
if k5<0,
k5 = abs(k5);
end
model.param.set('a1', k1);
model.param.set('b1', k2);
model.param.set('a4', k3);
model.param.set('b4', k4);
model.param.set('n', k5);
model.param.set('Q', '50[ml/min]', 'Flow rate of CO2');
model.param.set('V', '0.988[kV]', 'Voltage across the reactor');
model.param.set('I', '0.15[mA]', 'Current');
model.param.set('F', '96485[C/mol]', 'Faraday constant');
model.param.set('Ea1', '808.55[kJ/mol]', 'Activation energy for k1');
model.param.set('Ea4', '360.86[kJ/mol]', 'Activation energy for k4');
model.param.set('M_CO2', '44[g/mol]', 'Molecular mass of CO2');
model.param.set('M_H2O', '18[g/mol]', 'Molecular mass of H2O');
model.param.set('M_CO', '28[g/mol]', 'Molecular mass of CO');
model.param.set('M_O2', '32[g/mol]', 'Molecular mass of O2');
model.param.set('M_CH4', '16[g/mol]', 'Molecular mass of CH4');
% model.param.set('a1', '2.3*10^5[1/C]');
% model.param.set('b1', '0.05[1]', 'kinetic parameter for k1');
% model.param.set('a4', '4*10^2[m^3/mol/C]');
% model.param.set('b4', '0.01[1]', 'kinetic parameter for k4');
% model.param.set('n', '0.5[1]', 'kinetic parameter');
model.param.set('C0_CO2', '2.065e-5[mol/ml]');
model.param.set('C0_H2O', '4.191e-5[mol/ml]');

% Concentration of CO2
cCO2(1) = mphinterp(model, 'cCO2', 'coord', [0.0014;0;0.00556]);
cCO2(2) = mphinterp(model, 'cCO2', 'coord', [0.0014;0.000055;0.00556]);
cCO2(3) = mphinterp(model, 'cCO2', 'coord', [0.0014;0.000111;0.00556]);
cCO2(4) = mphinterp(model, 'cCO2', 'coord', [0.0038;0.000556]);
cCO2(5) = mphinterp(model, 'cCO2', 'coord', [0.0038;0.000055;0.00556]);
cCO2(6) = mphinterp(model, 'cCO2', 'coord', [0.0038;0.000111;0.00556]);
cCO2(7) = mphinterp(model, 'cCO2', 'coord', [0.0062;0.000556]);
cCO2(8) = mphinterp(model, 'cCO2', 'coord', [0.0062;0.000055;0.00556]);
cCO2(9) = mphinterp(model, 'cCO2', 'coord', [0.0062;0.000111;0.00556]);
cCO2_mod = mean([cCO2(1) cCO2(2) cCO2(3) cCO2(4) cCO2(5) cCO2(6) cCO2(7) cCO2(8) cCO2(9)]);

% Concentration of H2O
cH2O(1) = mphinterp(model, 'cH2O', 'coord', [0.0014;0;0.00556]);
cH2O(2) = mphinterp(model,'cH2O','coord',[0.0014;0.000055;0.00556]);
cH2O(3) = mphinterp(model,'cH2O','coord',[0.0014;0.00011;0.00556]);
cH2O(4) = mphinterp(model,'cH2O','coord',[0.0038;0.000055;0.00556]);
cH2O(5) = mphinterp(model,'cH2O','coord',[0.0038;0.000055;0.00556]);
cH2O(6) = mphinterp(model,'cH2O','coord',[0.0038;0.00011;0.00556]);
cH2O(7) = mphinterp(model,'cH2O','coord',[0.0062;0.000055;0.00556]);
cH2O(8) = mphinterp(model,'cH2O','coord',[0.0062;0.000055;0.00556]);
cH2O(9) = mphinterp(model,'cH2O','coord',[0.0062;0.00011;0.00556]);

cH2O_mod = mean([cH2O(1) cH2O(2) cH2O(3) cH2O(4) cH2O(5) cH2O(6) cH2O(7) cH2O(8) cH2O(9)]);

% Concentration of O2

\(cO2(1) = mphinterp(model,'cO2','coord',[0.0014;0;0.00556]);\)
\(cO2(2) = mphinterp(model,'cO2','coord',[0.0014;0.000055;0.00556]);\)
\(cO2(3) = mphinterp(model,'cO2','coord',[0.0014;0.00011;0.00556]);\)
\(cO2(4) = mphinterp(model,'cO2','coord',[0.0038;0;0.00556]);\)
\(cO2(5) = mphinterp(model,'cO2','coord',[0.0038;0.000055;0.00556]);\)
\(cO2(6) = mphinterp(model,'cO2','coord',[0.0038;0.00011;0.00556]);\)
\(cO2(7) = mphinterp(model,'cO2','coord',[0.0062;0.000055;0.00556]);\)
\(cO2(8) = mphinterp(model,'cO2','coord',[0.0062;0.000055;0.00556]);\)
\(cO2(9) = mphinterp(model,'cO2','coord',[0.0062;0.00011;0.00556]);\)

cO2_mod = mean([cO2(1) cO2(2) cO2(3) cO2(4) cO2(5) cO2(6) cO2(7) cO2(8) cO2(9)]);

% Concentration of CO

\(cCO(1) = mphinterp(model,'cCO','coord',[0.0014;0;0.00556]);\)
\(cCO(2) = mphinterp(model,'cCO','coord',[0.0014;0.000055;0.00556]);\)
\(cCO(3) = mphinterp(model,'cCO','coord',[0.0014;0.00011;0.00556]);\)
\(cCO(4) = mphinterp(model,'cCO','coord',[0.0038;0;0.00556]);\)
\(cCO(5) = mphinterp(model,'cCO','coord',[0.0038;0.000055;0.00556]);\)
\(cCO(6) = mphinterp(model,'cCO','coord',[0.0038;0.00011;0.00556]);\)
\(cCO(7) = mphinterp(model,'cCO','coord',[0.0062;0.000055;0.00556]);\)
\(cCO(8) = mphinterp(model,'cCO','coord',[0.0062;0.000055;0.00556]);\)
\(cCO(9) = mphinterp(model,'cCO','coord',[0.0062;0.00011;0.00556]);\)

\(cCO_mod = mean([cCO(1) cCO(2) cCO(3) cCO(4) cCO(5) cCO(6) cCO(7) cCO(8) cCO(9)]);\)

% Concentration of CH4

\(cCH4(1) = mphinterp(model,'cCH4','coord',[0.0014;0;0.00556]);\)
\(cCH4(2) = mphinterp(model,'cCH4','coord',[0.0014;0.000055;0.00556]);\)
\(cCH4(3) = mphinterp(model,'cCH4','coord',[0.0014;0.00011;0.00556]);\)
\(cCH4(4) = mphinterp(model,'cCH4','coord',[0.0038;0;0.00556]);\)
\(cCH4(5) = mphinterp(model,'cCH4','coord',[0.0038;0.000055;0.00556]);\)
\(cCH4(6) = mphinterp(model,'cCH4','coord',[0.0038;0.00011;0.00556]);\)
\(cCH4(7) = mphinterp(model,'cCH4','coord',[0.0062;0.000055;0.00556]);\)
\(cCH4(8) = mphinterp(model,'cCH4','coord',[0.0062;0.000055;0.00556]);\)
\(cCH4(9) = mphinterp(model,'cCH4','coord',[0.0062;0.00011;0.00556]);\)

\(cCH4_mod = mean([cCH4(1) cCH4(2) cCH4(3) cCH4(4) cCH4(5) cCH4(6) cCH4(7) cCH4(8) cCH4(9)]);\)

\(f = [cCO2_mod cH2O_mod cO2_mod cCO_mod cCH4_mod];\)

3. Build an intermediate program in Matlab

In order to optimize all the experimental data at single run, an intermediate program with a loop, objective function and experimental data has been created. The “for-end” loop
allows this program to read the simulated results sequentially. The objective function is sum of squares of differences between experimental concentrations and simulated concentrations.

The code for this intermediate program:

```matlab
function f = CO2Corona(k)
x = numel(k);
C_mod = zeros(14, x);

% Loop to call the simulated concentrations for each condition
for n = 1:14
    s1 = 'Concentration';
    s2 = num2str(n);
    s = strcat(s1, s2);
    fh = str2func(s);
    C_mod(n,:) = fh(k);
end

% Experimental data
C_exp = [20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;
         20.3169, 41.6873, 0.4094, 0.2208, 0.1111;];

% Objective function
f1 = (C_mod(1,1)-C_exp(1,1))^2+(C_mod(1,2)-C_exp(1,2))^2+(C_mod(1,3)-C_exp(1,3))^2+(C_mod(1,4)-
     C_exp(1,4))^2+(C_mod(1,5)-C_exp(1,5))^2;

f2 = (C_mod(2,1)-C_exp(2,1))^2+(C_mod(2,2)-C_exp(2,2))^2+(C_mod(2,3)-C_exp(2,3))^2+(C_mod(2,4)-
     C_exp(2,4))^2+(C_mod(2,5)-C_exp(2,5))^2;

f3 = (C_mod(3,1)-C_exp(3,1))^2+(C_mod(3,2)-C_exp(3,2))^2+(C_mod(3,3)-C_exp(3,3))^2+(C_mod(3,4)-
     C_exp(3,4))^2+(C_mod(3,5)-C_exp(3,5))^2;

f4 = (C_mod(4,1)-C_exp(4,1))^2+(C_mod(4,2)-C_exp(4,2))^2+(C_mod(4,3)-C_exp(4,3))^2+(C_mod(4,4)-
     C_exp(4,4))^2+(C_mod(4,5)-C_exp(4,5))^2;

f5 = (C_mod(5,1)-C_exp(5,1))^2+(C_mod(5,2)-C_exp(5,2))^2+(C_mod(5,3)-C_exp(5,3))^2+(C_mod(5,4)-
     C_exp(5,4))^2+(C_mod(5,5)-C_exp(5,5))^2;

f6 = (C_mod(6,1)-C_exp(6,1))^2+(C_mod(6,2)-C_exp(6,2))^2+(C_mod(6,3)-C_exp(6,3))^2+(C_mod(6,4)-
     C_exp(6,4))^2+(C_mod(6,5)-C_exp(6,5))^2;

f7 = (C_mod(7,1)-C_exp(7,1))^2+(C_mod(7,2)-C_exp(7,2))^2+(C_mod(7,3)-C_exp(7,3))^2+(C_mod(7,4)-
     C_exp(7,4))^2+(C_mod(7,5)-C_exp(7,5))^2;

f8 = (C_mod(8,1)-C_exp(8,1))^2+(C_mod(8,2)-C_exp(8,2))^2+(C_mod(8,3)-C_exp(8,3))^2+(C_mod(8,4)-
     C_exp(8,4))^2+(C_mod(8,5)-C_exp(8,5))^2;

f9 = (C_mod(9,1)-C_exp(9,1))^2+(C_mod(9,2)-C_exp(9,2))^2+(C_mod(9,3)-C_exp(9,3))^2+(C_mod(9,4)-
     C_exp(9,4))^2+(C_mod(9,5)-C_exp(9,5))^2;
```
\[
\begin{align*}
\text{f10} &= (C_{\text{mod}}(10,1) - C_{\text{exp}}(10,1))^2 + (C_{\text{mod}}(10,2) - C_{\text{exp}}(10,2))^2 + (C_{\text{mod}}(10,3) - C_{\text{exp}}(10,3))^2 + (C_{\text{mod}}(10,4) - C_{\text{exp}}(10,4))^2 + (C_{\text{mod}}(10,5) - C_{\text{exp}}(10,5))^2; \\
\text{f11} &= (C_{\text{mod}}(11,1) - C_{\text{exp}}(11,1))^2 + (C_{\text{mod}}(11,2) - C_{\text{exp}}(11,2))^2 + (C_{\text{mod}}(11,3) - C_{\text{exp}}(11,3))^2 + (C_{\text{mod}}(11,4) - C_{\text{exp}}(11,4))^2 + (C_{\text{mod}}(11,5) - C_{\text{exp}}(11,5))^2; \\
\text{f12} &= (C_{\text{mod}}(12,1) - C_{\text{exp}}(12,1))^2 + (C_{\text{mod}}(12,2) - C_{\text{exp}}(12,2))^2 + (C_{\text{mod}}(12,3) - C_{\text{exp}}(12,3))^2 + (C_{\text{mod}}(12,4) - C_{\text{exp}}(12,4))^2 + (C_{\text{mod}}(12,5) - C_{\text{exp}}(12,5))^2; \\
\text{f13} &= (C_{\text{mod}}(13,1) - C_{\text{exp}}(13,1))^2 + (C_{\text{mod}}(13,2) - C_{\text{exp}}(13,2))^2 + (C_{\text{mod}}(13,3) - C_{\text{exp}}(13,3))^2 + (C_{\text{mod}}(13,4) - C_{\text{exp}}(13,4))^2 + (C_{\text{mod}}(13,5) - C_{\text{exp}}(13,5))^2; \\
\text{f14} &= (C_{\text{mod}}(14,1) - C_{\text{exp}}(14,1))^2 + (C_{\text{mod}}(14,2) - C_{\text{exp}}(14,2))^2 + (C_{\text{mod}}(14,3) - C_{\text{exp}}(14,3))^2 + (C_{\text{mod}}(14,4) - C_{\text{exp}}(14,4))^2 + (C_{\text{mod}}(14,5) - C_{\text{exp}}(14,5))^2; \\
f &= \text{f1} + \text{f2} + \text{f3} + \text{f4} + \text{f5} + \text{f6} + \text{f7} + \text{f8} + \text{f9} + \text{f10} + \text{f11} + \text{f12} + \text{f13} + \text{f14};
\end{align*}
\]

4. Build a main program in Matlab

Open a new m. file and set the initial guess value. Then, use the syntax `fminsearch` to find the minimum value of objective function by varying kinetic parameters and set the options. Finally, run the major function and wait for the results.

The code for the major function:

```matlab
% fminsearch: find minimum of unconstrained multi-variable function using
% derivative-free method
clear all, format compact
global k0
%
% Initial guess
k0 = [2.3e5 0.05 400 0.01 0.5];
%
% Options setting
options = optimset('Display','iter','TolFun',0.1,'PlotFcns',@optimplotfval);
% k = reaction rate constant
% fval = value of objective function
% exitflag = describe the exit condition of fminsearch
% output = returns a structure output that contains information about the optimization
[k,fval,exitflag,output] = fminsearch('CO2Corona',k0,options);
```

References


