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Yu Miao for the degree of Master of Science in Chemical Engineering presented on May 21, 2013.

Title: <u>CO₂ Reduction in Aqueous-Ionic Liquid Solution in Microscale-Based Corona</u> <u>Reactor</u>

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Global warming problem is becoming an increasingly important environmental concern and CO_2 is considered as the major cause of global warming. Among various methods of CO_2 utilization, conversion of CO_2 to value added chemical products is the most attractive. In this study, a microscale-based corona reactor is introduced for reduction of CO_2 .

Two kinds of solvent were used in this study for absorbing CO_2 : DI-water and ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]). The latter one has a much higher solubility of CO_2 . After saturated with CO_2 , solution was introduced into the microreactor built around the concept of corona discharge. The corona was created through a significant potential difference between two graphite electrodes. The current that passed through two electrodes acted as a catalytic agent for the reduction of CO_2 .

The experiments were conducted at room temperature and at steady state. The ranges of the operating conditions were: mean residence time 5 to 100 (sec), thickness of spacer 200 and 500 (μ m), and voltage applied across the reactor 20 and 22.5 (V). Reactions happened in the bulk of the reactor and five main products were detected at the outlet stream: i) formic acid (HCOOH), ii) formaldehyde (HCHO), iii) methanol (CH₃OH), iv) methane (CH₄) and v) hydrogen (H₂). Among these compounds, formic acid, formaldehyde and methanol are intermediate products.

The conversion of CO_2 in aqueous solution can reach as high as 94.8% at mean residence time of 100 sec. Although in ionic liquid solution the conversion of CO_2 is much lower (19.3% at mean residence time of 100 sec), consumption of CO_2 in ionic liquid is 6-7 times larger than that in water when generating same volume of products.

A mathematical model reflecting geometry and flow conditions inside the microreactor was developed to simulate the process of CO_2 reduction. The model was solved numerically using COMSOL Multiphysics software package. The simulated results were optimized to fit the experimental data using COMSOL-Matlab LiveLink software package. Primary reaction rate constants for CO_2 reduction were predicted. The mathematical model was found to explain the experimental data pretty well.

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CO₂ Reduction in Aqueous-Ionic Liquid Solution in Microscale-Based Corona Reactor

by

Yu Miao

A THESIS

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

Yu Miao, Author

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LIST OF SYMBOLS

A_i	Analytical result of <i>i</i> th measurement;
Ā	Average of analytical results;
A _{max}	Maximum value of analytical results;
A_{min}	Minimum value of analytical results;
$A_{questionable}$	Questionable value of analytical results;
$A_{neighbour}$	Value of analytical results next to questionable value;
b	Intercept of the best fit line;
С	Total molar concentration of all species in the mixture (mol/m^3) ;
C_i	Molar concentration of species " i " (mol/m ³);
$C_{i,exp}$	Molar concentration of species " i " from experimental data (mol/m ³);
$C_{i,mod}$	Molar concentration of species " i " from COMSOL model (mol/m ³);
D_i	Diffusion Coefficient (m ² /sec);
d	Gap in Dixon's test;
F	Original objective function $((mol/m^3)^2)$;
<i>F_{new}</i>	New objective function $((mol/m^3)^2)$;
g_x	Gravity in x-direction (m/s ²);
<i>8</i> _y	Gravity in y-direction (m/s ²);
<i>8z</i>	Gravity in z-direction (m/s^2) ;
Н	Half height of the reactor (m);
k _B	Boltzmann's Constant (1.38×10 ⁻²³ J/K);
L	Length of the reactor (m);
M_1	Molecular weight of the solute (g/mol);

M_2	Molecular weight of the solvent (g/mol);
m	Slope of the best fit line;
Ν	Number of measurements (dimensionless);
N _A	Avogadro's constant $(6.02 \times 10^{23} \text{ mol}^{-1})$;
$N_{i,x}$	Molar flux of species " <i>i</i> " in x-direction (mol/m ² ·sec);
N _{i,y}	Molar flux of species " <i>i</i> " in y-direction (mol/m ² ·sec);
N _{i,z}	Molar flux of species " <i>i</i> " in z-direction (mol/m ² ·sec);
Р	Pressure at any point in the reactor (Pa);
P_0	Pressure at the inlet of the reactor (Pa);
P_L	Pressure at the outlet of the reactor (Pa);
Q	Q value in Dixon's test (dimensionless);
Q_{table}	Q value at different measurement number on Dixon's test table
	(dimensionless);
Q_V	(dimensionless); Flow rate (ml/hr);
Q_V R_i	(dimensionless); Flow rate (ml/hr); Rate of generation of species " <i>i</i> " per unit volume (mol/m ³ ·sec);
Q_V R_i r_1	(dimensionless); Flow rate (ml/hr); Rate of generation of species " <i>i</i> " per unit volume (mol/m ³ ·sec); Molecular radius of solute (Å);
Qv R _i r ₁ S/N	(dimensionless); Flow rate (ml/hr); Rate of generation of species " <i>i</i> " per unit volume (mol/m ³ ·sec); Molecular radius of solute (Å); Signal and noise ratio;
Qv R _i r ₁ S/N s _C	(dimensionless); Flow rate (ml/hr); Rate of generation of species " <i>i</i> " per unit volume (mol/m ³ ·sec); Molecular radius of solute (Å); Signal and noise ratio; Uncertainty in the concentration;
Q_V R_i r_1 S/N S_C S_y	(dimensionless); Flow rate (ml/hr); Rate of generation of species " <i>i</i> " per unit volume (mol/m ³ ·sec); Molecular radius of solute (Å); Signal and noise ratio; Uncertainty in the concentration;
Q_V R_i r_1 S/N S_C S_y S_m	(dimensionless); Flow rate (ml/hr); Rate of generation of species " <i>i</i> " per unit volume (mol/m ³ ·sec); Molecular radius of solute (Å); Signal and noise ratio; Uncertainty in the concentration; Uncertainty in the slope;
Q_V R_i r_1 S/N S_C S_y S_m S_r	<pre>(dimensionless); Flow rate (ml/hr); Rate of generation of species "i" per unit volume (mol/m³·sec); Molecular radius of solute (Å); Signal and noise ratio; Uncertainty in the concentration; Uncertainty in the slope; Uncertainty in the slope;</pre>
Q_V R_i r_1 S/N S_C S_y S_m S_r S_y	(dimensionless); Flow rate (ml/hr); Rate of generation of species "i" per unit volume (mol/m ³ ·sec); Molecular radius of solute (Å); Signal and noise ratio; Uncertainty in the concentration; Uncertainty in the slope; Uncertainty in regression; Uncertainty in regression;
Q_V R_i r_1 S/N S_C S_y S_m S_r S_y T	(dimensionless); Flow rate (ml/hr); Rate of generation of species " <i>i</i> " per unit volume (mol/m ³ ·sec); Molecular radius of solute (Å); Signal and noise ratio; Uncertainty in the concentration; Uncertainty in the concentration; Uncertainty in the slope; Uncertainty in regression; Uncertainty in regression; Engerature (K);

t_m	Mean residence time (sec);
Vvolume	Volume of the reactor (m^3) ;
V_1	Molar volume of solute (cm ³ /mol);
V _x	Velocity of solution in x-direction (m/s);
v_y	Velocity of solution in y-direction (m/s);
Vz	Velocity of solution in z-direction (m/s);
W	Width of the reactor (m);
w	Range in Dixon's test;
З	Tolerance on the objective function $((mol/m^3)^2)$;
μ	Viscosity of the solvent (Pa·s);
ρ	Density of the solvent (g/cm^3) ;
$ ho_1$	Density of the solute (g/cm^3) ;
σ	Standard deviation;
σ_m	Standard error (or standard deviation of the mean);
ϕ	Associate factor for the solvent in Wilke-Chang Correlation
	(dimensionless);

CO₂ Reduction in Aqueous-Ionic Liquid Solution in

Microscale-Based Corona Reactor

Chapter 1- Introduction and Background

1.1 Global Warming and Influence

When people talk about greenhouse gases and climate change, carbon dioxide usually gets the most attention. There are also some others, although CO₂ is the most important by far.¹ In 2011, CO₂ accounted for about 84% of all U.S. greenhouse gas emissions from human activities (see *Figure 1*)². Human activities are altering the carbon cycle--both by adding more CO₂ to the atmosphere and by influencing the ability of natural sinks, like forests, to remove CO₂ from the atmosphere. While CO₂ emissions come from a variety of natural sources, human-related emissions are responsible for the increase that has occurred in the atmosphere since the industrial revolution.³



Figure 1. U.S. Greenhouse Gas Emission from Human Activities in 2011²

The main human activity that emits CO_2 is the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes and land-use changes also emit CO_2 . The main sources of CO_2 emissions in

the United States are described below²:

• Electricity

Electricity is a significant source of energy in the United States and is used to power homes, business, and industry. The combustion of fossil fuels to generate electricity is the largest single source of CO_2 emissions in the nation, accounting for about 38% of total U.S. CO_2 emissions (See **Figure 2**). The type of fossil fuel used to generate electricity will emit different amounts of CO_2 . To produce a given amount of electricity, burning coal will produce more CO_2 than oil or natural gas.

• Transportation

The combustion of fossil fuels, such as gasoline and diesel to transport people and goods is the second largest source of CO_2 emissions, accounting for about 31% of total U.S. CO_2 emissions (See *Figure 2*). This category includes transportation sources such as highway vehicles, air travel, marine transportation, and rail.



Figure 2. U.S. Carbon Dioxide Emission (Categorized by Source)²

• Industry

Many industrial processes emit CO_2 through fossil fuel combustion. Several processes also produce CO_2 emissions through chemical reactions that do not involve combustion, for example, the production and consumption of mineral products such as cement, the production of metals such as iron and steel, and the production of chemicals. Various industrial processes accounted for about 14% of total U.S. CO_2 emissions (See *Figure 2*). Note that many industrial processes also use electricity and therefore indirectly cause the emissions from the electricity production.

Human activities have contributed substantially to climate change by adding CO_2 and other heat-trapping gases to the atmosphere. The pattern of steadily increasing concentrations of CO_2 is visible according to researchers' half-century measurements. The pre-industrial concentration of CO_2 was 280 parts per million. In 2005, that level, measured high above Mauna Loa, was 381 parts per million.¹ Currently, that level is 395 parts per million (See *Figure 3*).



Figure 3. Atmospheric CO₂ at Manua Loa Observatory¹

Besides the astonishing data, very dramatic changes taking place in the world around us is also evident: melting glaciers on the mountain and polar region increase sea levels; growing global temperature breaks all-time records for high temperatures in many cities; more and more unusually powerful hurricanes hit continents; changing rhythm of the seasons threats the survival of many species, etc.¹

1.2 CO₂ Utilization and Conversion

The utilization of CO₂ to produce value added products such as chemical products is an opportunity with growing benefits. CO₂ utilization includes the uses of CO₂ in both physical processes such as sequestration and chemical processes such as chemical synthesis. CO₂ conversion belongs to the second part and it refers to transformation of CO₂ to chemically different forms that contain carbon of CO₂ or that make use of active "oxygen atom" from CO₂.⁴ There are several motivations for producing chemicals from CO₂: (1) Not only is the resource truly renewable and cheap, but may also reduce liability to carbon taxes or cap-and-trade policies; (2) CO₂ is considered as a nontoxic feedstock that can replace toxic chemicals such as phosgene and isocyanates; (3) The successful development of an efficient system producing chemical products employing CO_2 could open new avenues to resource utilization; (4) The production of chemicals from CO_2 has a small, but positive impact on the global carbon balance; (5) The use of CO_2 as feedstock or co-reactant is a challenging opportunity which stimulates new approaches in industrial chemistry.⁵ Numerous routes for the conversion of CO₂ into chemical products are available, and they are described in open literature.⁶⁻¹⁸

There exist barriers and challenges for promoting CO_2 utilization, which include but are not limited to the following: 1) Costs of CO_2 capture, separation, purification, and transportation to user site; 2) Energy requirements of CO_2 chemical conversion; 3) Market size limitations, and lack of investment-incentives for CO_2 -based chemicals; and 4) Lack of socio-economical and political driving forces that facilitate enhanced CO_2 utilization.⁴

Accordingly, the following strategic considerations are proposed and may be helpful for future directions: 1) To produce useful chemicals and materials using CO_2 as a

co-reactant or co-feed; 2) To make use of CO_2 based on the unique physical or chemical properties of CO_2 ; 3) To replace a hazardous or less-effective substance in existing processes with CO_2 as an alternate medium or solvent or co-reactant or a combination of them; 4) To use CO_2 for energy recovery while reducing its emissions to the atmosphere by sequestration (storage); 5) To recycle CO_2 as C-source for chemicals and fuels; and 6) To convert CO_2 under geologic formation conditions into "new fossil" energies.⁴

1.3 State of Microtechnology

1.3.1 Definition

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 generally is performed in a hierarchic manner, comprising an assembly of units composed of subunits and so forth.¹⁹

Microtechnology contributes to amounts of fields including production of information, production of services and production of energy and bulk materials. The first two fields have already been fully developed and several applications have launched on the market.²⁰ Compared with them, production of energy and bulk materials is considered as a promising potential field for microtechnology.

1.3.2 Fundamental Advantages of Microreactors

Originating from chemical engineering principles, there are fundamental advantages associated with miniaturized reaction vessels that make microreactors more favorable than traditional systems.

1. Advantages Arising from Fundamental Phenomena

Intensification of Heat and Mass Transport

Due to short diffusional distances, conversion rates can be significantly enhanced in microsystems. This was exemplarily verified for the intensification of heat transfer of thermally coupled high-temperature reactions by recent calculations. For a given chemical process, using conventional technology and a microreactor, calculations predict that the amount of catalyst needed can be decreased by miniaturization by nearly a factor of 1000.¹⁹

Reduced Size

Due to the reduction of the linear dimensions, the volume of microreactors is significantly decreased compared to conventional large-scale reactors.¹⁹ Hardware mass can also be reduced by 5-50 times. Reduction of the size also contribute 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 m²/m³, whereas typical laboratory and production vessels usually do not exceed 1000 m²/m³ and 100 m²/m³. This increase not only benefits to heat transfer, but also can be utilized catalytic reactors.¹⁹

Other benefits arising from fundamental phenomena include changing chemical product distribution, lowering pressure drop, gravity independence, 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. 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 simply 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.¹⁹

Operating Robustness and Controllability

The numbering-up approach mentioned above also allows problems to be isolated and repaired. Compared with shutting down whole device to solve problems on 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. In addition, the numbering-up strategy allows simple and inexpensive replication of microreactor units, and avoids complexity and intensively increasing cost on 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 small-diameter channels have a larger surface-to-volume ratio and small volume, which can have a better control over temperature and other process conditions and can translate to lower stored energy. Besides, due to the small volume, small reactant and product quantities can guarantee the safety of the process. Even though a microreactor fails, the small amount of chemicals accidently released could be easily contained. All the features above illustrate that microreactors are promising devices for safe operations in manufacturing.

1.4 Corona Discharge

1.4.1 Physics of Corona Discharge

A corona discharge is an electrical discharge brought on by the ionization of a fluid surrounding a conductor that is electrically energized. The discharge will occur when the potential gradient of the electric field around the conductor is high enough to form a conductive region, but not high enough to cause electrical breakdown or arcing to nearby objects. This high potential gradient can be created across a neutral fluid (as a gas, air; as a liquid, any organic alkane suffices) by ionizing the fluid and creating plasma around the electrode.²¹

The formation process of corona discharge is: 1) A neutral atom or molecule is ionized in a strong electric field by a natural environmental event (in our case, being struck by electrons in the current), to create a positive ion and a free electron; 2) The electric field accelerates these oppositely charged particles in opposite directions, separating them and preventing their recombination; 3) Due to a much higher charge/mass ratio, the electron has a higher velocity than the ion. When it gains enough energy from the field, it will strike another neutral atom or molecule and ionize it, knocking out another electron and creating another positive ion. These electrons collide with more atoms or molecules, in a chain reaction process called electron avalanche; 4) When there is enough electrons in the field, the recombination of electrons and positive ions will occur, creating a glow discharge. ²² This formation process can be shown in *Figure 4*.



Figure 4. Formation Process of Corona Discharge

Coronas can be divided into positive and negative. This is determined by the polarity of the voltage on the highly-curved electrode. If the curved electrode is positive with respect to the flat electrode, then it is positive corona otherwise it is negative corona if negative. The physical properties of positive and negative coronas are strikingly different: a positive corona is manifested as a uniform plasma while a negative corona is manifested in a non-uniform corona; a positive corona appears a little smaller than corresponding negative corona with the same geometry and voltages; a positive corona has much lower density of free electrons compared to a negative corona; the electrons in a positive corona are concentrated close to the surface of the curved conductor while many electrons in a negative corona are in the outer area; a positive corona generates much less ozone than the corresponding negative corona, etc.²³

Several materials can be used as electrodes to create positive corona, such as platinum²⁴, stainless steel^{25,26}, nickel-chromium²⁴ and carbon^{27,28}. Different geometries of the electrodes have been studied, including wire-to-plate²⁴, ring-to-cylinder²⁵ and parallel flat plates.²⁶⁻²⁸ In this study, carbon parallel flat plate electrodes are used to create coronas.

1.4.2 Application of Corona Discharge

Applications for corona discharge processes have existed for over a hundred years. It has been used in several commercial ways and is gaining attention for use in new applications. This technology has been used in many fields: electrostatic precipitation, electrophotography, static control in semiconductor manufacture, ionization instrumentation, control of acid gases from combustion sources, destruction of impurity compounds, and generation of ozone.²⁹ In this study, this technology is used for reducing greenhouse gas CO₂.

Currently, a majority of the research has been performed on applying the corona discharge for removal of organic/inorganic compounds. Mededovic et al. applied aqueous-phase pulsed corona discharge to catalyzed decomposition of hydrogen peroxide.²⁴ Sugiarto et al. reported their success on degradation of complex organic dyes by pulsed streamer corona discharge in water using a ring-to-cylinder electrode system.²⁵ Kirkpatrick et al. stated that gas phase pulsed streamer corona discharge can be used for chlorinated organic compound removal.²⁷ Lukes et al. suggested a gas-liquid corona discharge reactor for degrading of phenol.²⁸

Except applying corona discharge directly into chemical reactions, using this technology in the presence of some catalysts is also attractive for reduction of chemical components, especially carbon dioxide. Bozogzadeh et al. reported to use

tungsten wire-to-plate electrodes for CO_2 reforming of CH_4 with alumina supported Ni catalysts in gas phase.³⁰ Liu et al. reported to use stainless steel needle-to-plate electrodes for CO_2 reduction in the presence of NaY zeolite.³¹

Although there is no open literature about applying corona discharge for CO_2 reduction in the absence of catalyst, the applications above suggest that there is a possibility corona discharge can be used for CO_2 .

1.5 Ionic Liquid

The definition of ionic liquid is a molten organic salt with a melting point below 100°C and a high degree of asymmetry that frustrates packing and thus inhibits crystallization. The possible choices of cation and anion that will result in the formation of ionic liquids are numerous. Examples of five well-known classes of ionic liquids are shown in *Figure 5*. The anion (X⁻) can be any of a variety of species: nitrate (NO₃⁻), acetate (CH₃CO₂⁻), trifluoroacetate (CF₃CO₂⁻), tetrafluoroborate (BF₄⁻), triflate (CF₃SO₃⁻), hexafluorophosphate (PF₆⁻), bis(trifluoromethylsulfonyl)imide ((CF₃SO₂)₂N⁻) and halide (Cl⁻, Br⁻, Γ). The substituents on the cations (the "R" groups) are typically alkyl chains, but can contain any of a variety of other functional group as well (fluoroalkyl, alkenyl, methoxy, etc.). The properties of ionic liquids can be tailored by judicious selection of cation, anion, and substituents.³²



Figure 5. Five Well-known Classes of Ionic Liquids

The traditional liquid solvents are remarkably similar in one respect: they all have a relatively narrow liquidus region, ranging from 75 to around 200°C, which means that

they are all relatively volatile at process conditions. Besides this efficiency problem, the emissions of volatile organic compounds (VOCs) also linked to negative effects on environment. To help people meet the twin challenges of efficiency and environmental friendly chemical processing, room temperature ionic liquids (or simply "ionic liquids") become a key ally. This new class of compounds emerging in the last ten years acts much like good organic solvents, dissolving both polar and nonpolar species. Their most intriguing feature is that they have essentially no vapor pressure, which means they do not evaporate and cannot lead to fugitive emissions. Many of them are liquids over incredibly large temperature ranges, from below ambient to over 300 to 400°C, which allows them to be used under unique processing conditions. ³²

Another attraction of Ionic liquids is their relatively high solubility for CO_2 unlike in a non-basic aqueous system. Blath et al.^{33,34} and Muldoon et al.³⁵ reported Henry's Law constants for CO_2 dissolution in different kinds of ionic liquids at 60°C, which are summarized in *Table 1*. Smaller values of the Henry's law constant correspond to higher solubility. It is obvious that all the ionic liquids have higher solubility of CO_2 than water.

Ionic Liquid or Water	Henry's Law Constant (bar)	
[EMIM][OAc]	8.33 ³³	
[EMIM][BF ₄]	154.54 ³⁴	
[BMIM][NTf ₂]	52.93 ³⁴	
[BMIM][BF ₄]	123.0 ³⁴	
[HMIM][ACE]	113.1 ³⁵	
[HMIM][SAC]	132.2 ³⁵	
H ₂ O	3850.59 ³⁶	

Table 1. Henry's Law Constants for CO2 Dissolution in Different Kinds of IonicLiquids at 60°C

Except higher solubility, ionic liquids have another advantage. Rosen et al.³⁷ reported that some ionic liquids (e.g. [EMIM][BF₄] and [BMIM][BF₄]) can trap CO₂ by forming a molecular complex, which can lower the electrode potential required to convert CO₂. This is because the activation energy required to form the molecular complex (EMIM⁺-(CO₂)⁻ and BMIM⁺-(CO₂)⁻ in the paper) is lower than the energy required to form (CO₂)⁻ without stabilization through the cation, and the formation of the (CO₂)⁻ intermediate is the rate determining step, as shown in *Figure 6*.



Figure 6. A Schematic of How the Free Energy of the System Changes During the Reaction in Water (Solid Line) and EMIM-BF₄ or BMIM-BF₄ (Dashed Line)³⁷

In this study, ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]), as illustrated in *Figure 7*, is used as solvent. The Henry's law constants for CO₂, CH₄ and H₂ in water and [BMIM][BF₄] at room temperature are shown in *Table 2*. Although it may not be the best ionic liquid for absorbing CO₂, it is definitely better than water in this field because its Henry's Law constant is still much smaller than water and thus solubility of CO₂ in it is higher than that in water. Besides, [BMIM]⁺ cation can have an interaction with CO₂ anion radical to form BMIM⁺-(CO₂)⁻ intermediate.



Figure 7. Chemical Structure of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄])

Table 2. Henry's Law Constants for CO2, CH4 and H2 in Water and [BMIM][BF4]at Room Temperature (Unit: (L·atm)/mol)

Solvent Species	Water	[BMIM][BF4]
CO ₂	29.41 ³⁶	1.01^{38}
CH ₄	714.29 ³⁶	17.35 ³⁹
H ₂	1282.05 ³⁶	333.33 ⁴⁰
Chapter 2- Thesis Goal and Objectives

2.1 Goal

The principal Goal of this Project is to evaluate the feasibility of corona microscale-based technology for the conversion of CO_2 (dissolved in water and ionic liquids) into various chemical products.

2.2 Objectives

The main objectives of this Project are:

- Design, manufacture, construct and operate a microscale-based reactor system for conversion of CO₂ in water and ionic liquids into chemical products.
- Determine experimentally the performance envelope of a cell carrying out the corona discharge reduction of CO₂ in water and wet ionic liquids (5% water w/v).
- Determine the reaction rate constants in the process of corona discharge reduction of CO₂.

Chapter 3- Theoretical Background and Tools

3.1 Mathematical Model

3.1.1 Momentum Balance



Figure 8. Momentum Balance in the Corona Microreactor

- 1. Assumptions
 - (1) The fluid is Newtonian and incompressible
 - (2) The flow is laminar and isothermal

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

(4) No velocity in y and z direction, $v_y = 0$, $v_z = 0$

(5) Velocity doesn't change along the z direction,
$$\frac{\partial v_x}{\partial z} = 0$$

- (6) Neglect gravity, $g_x = g_y = g_z = 0$
- 2. Continuity Equation

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0 \Longrightarrow \frac{\partial v_x}{\partial x} = 0$$

3. Navier-Stokes Equations

Apply Navier-Stokes Equations in rectangular coordinates,

In *x* direction,

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

In y direction,

$$\rho \left[\frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \right] = -\frac{\partial P}{\partial y} + \mu \left[\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_y}{\partial z^2} \right] + \rho g_y$$

In z direction,

$$\rho \left[\frac{\partial v_z}{\partial t} + v_y \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \right] = -\frac{\partial P}{\partial z} + \mu \left[\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} + \frac{\partial^2 v_z}{\partial z^2} \right] + \rho g_z$$

After simplification, Navier-Stokes Equations become

$$\frac{\partial P}{\partial x} = \mu \frac{\partial^2 v_x}{\partial y^2}, \quad \frac{\partial P}{\partial y} = 0, \quad \frac{\partial P}{\partial z} = 0$$

4. Boundary Conditions

5. Velocity Profile

$$\frac{\partial P}{\partial x} = \mu \frac{\partial^2 v_x}{\partial y^2} = \text{Constant}$$
$$\frac{\partial P}{\partial x} = \text{Constant} \Rightarrow \int_{P_0}^{P_L} dP = \text{Constant} \cdot \int_0^L dx \Rightarrow \text{Constant} = \frac{P_L - P_0}{L}$$
$$\mu \frac{\partial^2 v_x}{\partial y^2} = \text{Constant} = \frac{P_L - P_0}{L} \Rightarrow \frac{\partial^2 v_x}{\partial y^2} = \frac{P_L - P_0}{\mu L} \Rightarrow \frac{\partial v_x}{\partial y} = \frac{P_L - P_0}{\mu L} \text{ y} + \text{Constant } 1$$

@
$$y = 0$$
, $\frac{\partial v_x}{\partial y} = 0 \Rightarrow \text{Constant } 1 = 0 \Rightarrow \frac{\partial v_x}{\partial y} = \frac{P_L - P_0}{\mu L} y \Rightarrow v_x = \frac{P_L - P_0}{\mu L} \frac{y^2}{2} + \text{Constant } 2$

@
$$y = H$$
, $v_x = 0 \Longrightarrow \text{Constant } 2 = -\frac{P_L - P_0}{\mu L} \frac{H^2}{2}$

The expression of the velocity profile would be

$$v_{x}(y) = \frac{P_{L} - P_{0}}{\mu L} \frac{y^{2} - H^{2}}{2}$$

3.1.2 Material Balance



Figure 9. Material Balance in the Corona Microreactor

1. Assumptions

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

(2) No convection or diffusion in z direction, $v_z = 0, N_{i,z} = 0$

(3) Steady state process,
$$\frac{C_i|_{t+\Delta t} - C_i|_t}{\Delta t} = 0$$

(4) Dilute solution,
$$\frac{C_i}{C} = 0$$

2. Material Balance Equation

Governing equation: IN - OUT + GENERATION = ACCUMULATION $v_x \cdot C_i \cdot \Delta y \Delta z \Delta t \Big|_x - v_x \cdot C_i \cdot \Delta y \Delta z \Delta t \Big|_{x+\Delta x}$ Convection In – Convection Out: $+ v_y \cdot C_i \cdot \Delta x \Delta z \Delta t \Big|_y - v_y \cdot C_i \cdot \Delta x \Delta z \Delta t \Big|_{y+\Delta y}$ $+ v_z \cdot C_i \cdot \Delta x \Delta y \Delta t \Big|_z - v_z \cdot C_i \cdot \Delta x \Delta y \Delta t \Big|_{z+\Delta z}$

$$N_{i,x} \cdot \Delta y \Delta z \,\Delta t \big|_{x} - N_{i,x} \cdot \Delta y \Delta z \,\Delta t \big|_{x+\Delta x}$$

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

Generation: $R_i \cdot \Delta x \Delta y \Delta z \Delta t$

Accumulation:
$$C_i \cdot \Delta x \Delta y \Delta z \Big|_{t+\Delta t} - C_i \cdot \Delta x \Delta y \Delta z \Big|_t$$

The material balance becomes:

$$v_{x} \cdot C_{i} \cdot \Delta y \Delta z \,\Delta t \big|_{x} - v_{x} \cdot C_{i} \cdot \Delta y \Delta z \,\Delta t \big|_{x+\Delta x} + N_{i,x} \cdot \Delta y \Delta z \,\Delta t \big|_{x} - N_{i,x} \cdot \Delta y \Delta z \,\Delta t \big|_{x+\Delta x} + N_{i,y} \cdot \Delta x \Delta z \,\Delta t \big|_{y} - N_{i,y} \cdot \Delta x \Delta z \,\Delta t \big|_{y+\Delta y} + R_{i} \cdot \Delta x \Delta y \Delta z \Delta t = 0$$

Divide by $\Delta x \Delta y \Delta z \Delta t$, and take the limit as they approach zero:

$$\frac{\partial}{\partial x} \left(-v_x \cdot C_i \right) - \frac{\partial N_{i,x}}{\partial x} - \frac{\partial N_{i,y}}{\partial y} + R_i = 0$$

3. General Flux Equation

The general flux equation for a dilute mixture was adapted to this system:

$$N_i = -D_i \nabla C_i + \frac{C_i}{C} \sum_{i=1}^n N_i$$

Combine material balance and flux equation to develop a partial differential expression for C_i :

$$\frac{\partial}{\partial x} \left(-\upsilon_x \cdot C_i \right) - \frac{\partial}{\partial x} \left(-D_i \frac{\partial C_i}{\partial x} \right) - \frac{\partial}{\partial y} \left(-D_i \frac{\partial C_i}{\partial y} \right) + R_i = 0$$

4. Mass Transfer Partial Differential Equation and Boundary Conditions

Because v_x is function of y only and D_i is constant, this partial differential equation becomes:

$$\boxed{-\upsilon_x \frac{\partial C_i}{\partial x} + D_i \frac{\partial^2 C_i}{\partial x^2} + D_i \frac{\partial^2 C_i}{\partial y^2} + R_i = 0}$$

The following boundary conditions were chosen for the microreactor:

5. Diffusion Coefficients

The values of diffusion coefficients for CO₂, CH₄ and H₂ in water at room temperature are found in Table 5.2-1 from E.L.Cussler's *Diffusion: Mass Transfer in Fluid System*⁴¹ and the values for the other three species in water are calculated using Wilke-Chang Correlation and all the species in ionic liquid BMIM-BF₄ are calculated using Stokes-Einstein Equation (See *Appendix A*).

3.1.3 Mechanism of Reactions and Simplifications

- 1. Reactions with Water as Solvent
- A. Summary of Mechanism of Reactions

Step 1: When the electrodes in the corona reactor are charged, the water modecules will absorb emitted energy to generate water ions (H_2O^+) , electrons (e^-) , hydrogen radicals (H^*) and hydroxyl radicals (OH^*) just as shown in Eq1 and Eq2.

(1)
$$e_V^- + H_2 O \xrightarrow{k_1} H_2 O^+ + 2e^-$$
 Eq1



Figure 10. Mechanism of Corona Discharge Reduction of CO₂, Step 1

Step 2: Water ions combine with water modecules to produce hydronium ions (H_3O^+) and hydroxyl radicals (OH^*) as shown in Eq3. Subsequently, two hydroxyl radical (OH^*) can produce hydrogen peroxide (H_2O_2) , which is also reduced by electron (e^-) to generate hydroxyl anion (OH) and hydroxyl radical (OH^*) . And hydroxyl anion (OH) combines with hydronium ion (H_3O^+) to generate water molecules (H_2O) respectively as shown from Eq4 to Eq7. When CO₂ is dissolved in water it gives rise to hydrogen carbonate (H_2CO_3) which could provide proton and carbonate ion $(CO_3^{2^-})$ as shown in Eq8 and Eq9. The reactions described in Eq8 and Eq9 could be omitted due to the low solubility of CO₂ in water - 0.03 M at ambient conditions.

(3)
$$H_2O^+ + H_2O \xrightarrow{k_3} H_3O^+ + OH^*$$
 Eq3

$$(4) \ 2OH^* \xrightarrow{k_4} H_2O_2$$
 Eq4

(5)
$$H^* + OH^* \xrightarrow{k_5} H_2O$$
 Eq5

(6)
$$H_2O_2 + e^- \xrightarrow{k_6} OH^* + OH^-$$
 Eq6

(7)
$$H_3O^+ + OH^- \xrightarrow{k_7} 2H_2O$$
 Eq7

(8)
$$CO_2 + H_2O \xleftarrow{k_8}{k_{-8}} H_2CO_3$$
 Eq8

Eq2



Figure 11. Mechanism of Corona Discharge Reduction of CO₂, Step 2

Step 3: The following reactions will take place in the bulk of the fluid, all involving electron transfer. First, hydronium ion (H_3O^+) and electron (e^-) react to produce hydrogen radical (H^*) and water (H_2O) . Subsequently, two hydrogen radicals (H^*) combine to yield hydrogen molecules (H_2) as shown in Eq10 and Eq11. Then, CO₂ is reduced to yield CO₂ anion radicals (CO_2^{*-}) which react with electron (e^-) , hydronium ion (H_3O^+) and hydrogen radical (H^*) to yield formic acid (HCOOH) as shown from Eq12 to Eq14. Afterwards, the series of the reaction involving electron, hydronium ion and hydrogen radical lead to the formation of formaldehyde (HCHO) and methanol (CH_3OH) as shown from Eq15 to Eq22. Finally, the last reaction in this series is reaction of methanol (CH_3OH) and two hydrogen radicals (H^*) to yield methane (CH_4) as shown in Eq23 and Eq24.

- (10) $H_3O^+ + e^- \xrightarrow{k_{10}} H^* + H_2O$ Eq10
- (11) $2H^* \xrightarrow{k_{11}} H_2$ Eq11
- (12) $CO_2 + e^- \xrightarrow{k_{12}} O = C^* O^-$ Eq12

Eq9

(13)
$$O = C^* - O^- + H_3 O^+ \xrightarrow{k_{13}} O = C^* - OH + H_2 O$$
 Eq13

(14)
$$O = C^* - OH + H^* \xrightarrow{k_{14}} O = CH - OH$$
 Eq14

(15)
$$O = CH - OH + e^{-\frac{k_{15}}{2}} OH - HC^* - O^-$$
 Eq15

(16)
$$OH - HC^* - O^- + H_3O^+ \xrightarrow{k_{16}} OH - HC^* - OH + H_2O$$
 Eq16

(17)
$$OH - HC^* - OH + e^- \xrightarrow{k_{17}} OH - C^{*(-)}H - OH$$
 Eq17

(18)
$$OH - C^{*(-)}H - OH + H_3O^+ \xrightarrow{k_{18}} OH - CH_2 - OH + H_2O$$
 Eq18

(19)
$$OH - CH_2 - OH \xrightarrow{k_{19}} H_2O + HCHO$$
 Eq19

(20)
$$HCHO + e^- \xrightarrow{k_{20}} HC^*H - O^-$$
 Eq20

(21)
$$HC^*H - O^- + H_3O^+ \xrightarrow{k_{21}} HC^*H - OH + H_2O$$
 Eq21

(22)
$$HC^*H - OH + H^* \xrightarrow{k_{22}} CH_3OH$$
 Eq22

(23)
$$CH_3OH + H^* \xrightarrow{k_{23}} C^*H_3 + H_2O$$
 Eq23

(24)
$$C^*H_3 + H^* \xrightarrow{k_{24}} CH_4$$
 Eq24



Figure 12. Mechanism of Corona Discharge Reduction of CO_2 , Step 3

B. Differential Equations

(25)Concentration of carbon dioxide, CO_2

$$\frac{d}{dt} [CO_2] = -k_{12} [e^-] [CO_2] - k_8 [CO_2] [H_2O] + k_{-8} [H_2CO_3]$$
Eq25

(26)Concentration of hydrogen, H_2

$$\frac{d}{dt}[H_2] = k_{11}[H^*]^2$$
 Eq26

(27) Concentration of formic acid, HCOOH

$$\frac{d}{dt}[HCOOH] = k_{14}[H^*][O = C^* - OH] - k_{15}[e^-][HCOOH]$$
Eq27

(28) Concentration of formaldehyde, HCHO

$$\frac{d}{dt}[HCHO] = k_{19}[OH - CH_2 - OH] - k_{20}[e^-][HCHO]$$
Eq28

(29)Concentration of methanol, CH₃OH

$$\frac{d}{dt} [CH_3OH] = k_{22} [HC^*H - OH] [H^*] - k_{23} [H^*] [CH_3OH]$$
Eq29

(30)Concentration of methane, CH_4

$$\frac{d}{dt}[CH_4] = k_{24}[C^*H_3][H^*]$$
Eq30

(31)Concentration of holes, e

$$\frac{d}{dt} \Big[e^{-} \Big] = 2k_1 V \Big[H_2 O \Big] + k_2 V \Big[H_2 O \Big] - k_6 \Big[e^{-} \Big] \Big[H_2 O_2 \Big] - k_{10} \Big[H_3 O^{+} \Big] \Big[e^{-} \Big] - k_{12} \Big[CO_2 \Big] \Big[e^{-} \Big] \\ - k_{15} \Big[HCOOH \Big] \Big[e^{-} \Big] - k_{17} \Big[OH - HC^* - OH \Big] \Big[e^{-} \Big] - k_{20} \Big[e^{-} \Big] \Big[HCHO \Big]$$

(32)Concentration of electrons, H^*

$$\frac{d}{dt} \begin{bmatrix} H^* \end{bmatrix} = k_2 V \begin{bmatrix} H_2 O \end{bmatrix} + k_{10} \begin{bmatrix} H_3 O^+ \end{bmatrix} \begin{bmatrix} e^- \end{bmatrix} - k_5 \begin{bmatrix} H^* \end{bmatrix} \begin{bmatrix} OH^* \end{bmatrix} - k_{11} \begin{bmatrix} H^* \end{bmatrix}^2 -k_{14} \begin{bmatrix} H^* \end{bmatrix} \begin{bmatrix} O = C^* - OH \end{bmatrix} - k_{22} \begin{bmatrix} HC^*H - OH \end{bmatrix} \begin{bmatrix} H^* \end{bmatrix}$$
Eq32
$$-k_{23} \begin{bmatrix} H^* \end{bmatrix} \begin{bmatrix} CH_3 OH \end{bmatrix} - k_{24} \begin{bmatrix} C^*H_3 \end{bmatrix} \begin{bmatrix} H^* \end{bmatrix}$$

(33)Concentration of water ion, H_2O^+

$$\frac{d}{dt} \left[H_2 O^+ \right] = k_1 V \left[H_2 O \right] - k_3 \left[H_2 O^+ \right] \left[H_2 O \right]$$
Eq33

(34)Concentration of hydronium ion, H_3O^+

$$\frac{d}{dt} \begin{bmatrix} H_3 O^+ \end{bmatrix} = k_3 \begin{bmatrix} H_2 O^+ \end{bmatrix} \begin{bmatrix} H_2 O \end{bmatrix} - k_7 \begin{bmatrix} H_3 O^+ \end{bmatrix} \begin{bmatrix} O H^- \end{bmatrix} - k_{10} \begin{bmatrix} H_3 O^+ \end{bmatrix} \begin{bmatrix} e^- \end{bmatrix} - k_{13} \begin{bmatrix} H_3 O^+ \end{bmatrix} \begin{bmatrix} O = C^* - O^- \end{bmatrix} - k_{16} \begin{bmatrix} H_3 O^+ \end{bmatrix} \begin{bmatrix} O H - H C^* - O^- \end{bmatrix} - k_{18} \begin{bmatrix} H_3 O^+ \end{bmatrix} \begin{bmatrix} O H - C^{*(-)} H - O H \end{bmatrix} - k_{21} \begin{bmatrix} H_3 O^+ \end{bmatrix} \begin{bmatrix} H C^* H - O^- \end{bmatrix} Eq34$$

(35)Concentration of $O=C^*-O^-$

$$\frac{d}{dt} \Big[O = C^* - O^- \Big] = k_{12} \Big[CO_2 \Big] \Big[e^- \Big] - k_{13} \Big[H_3 O^+ \Big] \Big[O = C^* - O^- \Big]$$
Eq35

(36)Concentration of $O=C^*-OH$

$$\frac{d}{dt} \Big[O = C^* - OH \Big] = k_{13} \Big[H_3 O^+ \Big] \Big[O = C^* - O^- \Big] - k_{14} \Big[H^* \Big] \Big[O = C^* - OH \Big] \quad \text{Eq36}$$

(37)Concentration of $OH-HC^*-O^-$

$$\frac{d}{dt}\left[OH - HC^* - O^-\right] = k_{15}\left[HCOOH\right]\left[e^-\right] - k_{16}\left[H_3O^+\right]\left[OH - HC^* - O^-\right] \quad \text{Eq37}$$

(38)Concentration of OH-HC*-OH

$$\frac{d}{dt} \left[OH - HC^* - OH \right] = k_{16} \left[H_3 O^+ \right] \left[OH - HC^* - O^- \right] - k_{17} \left[OH - HC^* - OH \right] \left[e^- \right]$$
Eq38

(39)Concentration of $OH-C^{*(-)}H-OH$

$$\frac{d}{dt}\left[OH - C^{*(-)}H - OH\right] = k_{17}\left[OH - HC^* - OH\right]\left[e^{-}\right] - k_{18}\left[H_3O^+\right]\left[OH - C^{*(-)}H - OH\right]\right]$$

(40)Concentration of OH-CH₂-OH

$$\frac{d}{dt} \left[OH - CH_2 - OH \right] = k_{18} \left[H_3 O^+ \right] \left[OH - C^{*(-)}H - OH \right] - k_{19} \left[OH - CH_2 - OH \right]$$
Eq40

(41)Concentration of HC^*H-O^-

$$\frac{d}{dt} \left[HC^*H - O^- \right] = k_{20} \left[e^- \right] \left[HCHO \right] - k_{21} \left[H_3O^+ \right] \left[HC^*H - O^- \right]$$
Eq41

(42)Concentration of *HC*H–OH*

$$\frac{d}{dt} \left[HC^*H - OH \right] = k_{21} \left[H_3O^+ \right] \left[HC^*H - O^- \right] - k_{22} \left[HC^*H - OH \right] \left[H^* \right]$$
Eq42

(43)Concentration of C^*H_3

$$\frac{d}{dt} \left[C^* H_3 \right] = k_{23} \left[H^* \right] \left[CH_3 OH \right] - k_{24} \left[C^* H_3 \right] \left[H^* \right]$$
Eq43

(44)Concentration of hydrogen peroxide, H_2O_2

$$\frac{d}{dt} \begin{bmatrix} H_2 O_2 \end{bmatrix} = k_4 \begin{bmatrix} OH^* \end{bmatrix}^2 - k_6 \begin{bmatrix} e^- \end{bmatrix} \begin{bmatrix} H_2 O_2 \end{bmatrix}$$
Eq44

(45)Concentration of hydroxyl radical, OH^*

$$\frac{d}{dt} \begin{bmatrix} OH^* \end{bmatrix}$$

$$= k_{26}V \begin{bmatrix} H_2O \end{bmatrix} + k_{27} \begin{bmatrix} H_2O^+ \end{bmatrix} \begin{bmatrix} H_2O \end{bmatrix} - k_{28} \begin{bmatrix} OH^* \end{bmatrix}^2 - k_{29} \begin{bmatrix} OH^* \end{bmatrix} \begin{bmatrix} H^* \end{bmatrix} + k_{30} \begin{bmatrix} e^- \end{bmatrix} \begin{bmatrix} H_2O_2 \end{bmatrix}$$
Eq45

C. Assumptions

In order to simplify the differential equations above, we made the following assumptions:

(a) Reduction in the corona reactor is completed via e^{-} , H_3O^{+} and H^{*} attack on CO₂

(b) The concentration of e^- is constant at steady state, and according to Quasi-Steady-State assumption, their formation rates can be set equal to zero

$$\frac{d}{dt} \left[e^{-} \right] = 0$$

(c) If a Quasi-Steady-State assumption is invoked, the concentrations of all radicals and unstable intermediate compounds are constant at steady-state

$$\frac{d}{dt} \begin{bmatrix} H^* \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} H_2 O^+ \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} H_3 O^+ \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} H_2 O_2 \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} O = C^* - O^- \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} O = C^* - OH \end{bmatrix}$$
$$= \frac{d}{dt} \begin{bmatrix} OH - HC^* - O^- \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} OH - HC^* - OH \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} OH - C^{*(-)} H - OH \end{bmatrix}$$
$$= \frac{d}{dt} \begin{bmatrix} OH - CH_2 - OH \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} HC^* H - O^- \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} HC^* H - OH \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} C^* H_3 \end{bmatrix} = 0$$

(d) The concentration of H_2O^+ and e^- are equal⁴²

$$\left[H_2O^+\right] = \left[e^-\right]$$

(e) Almost all the H_3O^+ is used to produce H^*

$$k_7 \Big[H_3 O^+ \Big] \Big[OH^- \Big] \ll k_{10} \Big[H_3 O^+ \Big] \Big[e^- \Big]$$

(f) Almost all the CO₂ is used to produce hydro carbonates instead of carbonic acid

$$k_{12} [e^{-}] [CO_{2}] \gg k_{8} [CO_{2}] [H_{2}O] - k_{-8} [H_{2}CO_{3}]$$

D. Simplifications of Differential Equations

The assumptions (a)-(f) are applied to the rate equations Eq25 through Eq45.

(46) Apply assumption (c) and (d) into equation Eq33;

$$\frac{d}{dt} \Big[H_2 O^+ \Big] = k_1 V \Big[H_2 O \Big] - k_3 \Big[H_2 O^+ \Big] \Big[H_2 O \Big] = 0$$
$$\Rightarrow \Big[e^- \Big] = \Big[H_2 O^+ \Big] = \frac{k_1 V}{k_3}$$
Eq46

(47) Apply assumption (c) into equation Eq35;

$$\frac{d}{dt} \Big[O = C^* - O^- \Big] = k_{12} \Big[CO_2 \Big] \Big[e^- \Big] - k_{13} \Big[H_3 O^+ \Big] \Big[O = C^* - O^- \Big] = 0$$

$$\Rightarrow k_{12} \Big[CO_2 \Big] \Big[e^- \Big] = k_{13} \Big[H_3 O^+ \Big] \Big[O = C^* - O^- \Big]$$
Eq47

(48) Apply assumption (c) into equation Eq36;

$$\frac{d}{dt} \Big[O = C^* - OH \Big] = k_{13} \Big[H_3 O^+ \Big] \Big[O = C^* - O^- \Big] - k_{14} \Big[H^* \Big] \Big[O = C^* - OH \Big] = 0$$

$$\Rightarrow k_{13} \Big[H_3 O^+ \Big] \Big[O = C^* - O^- \Big] = k_{14} \Big[H^* \Big] \Big[O = C^* - OH \Big]$$
Eq48

(49) Apply assumption (c) into equation Eq37;

$$\frac{d}{dt} \Big[OH - HC^* - O^- \Big] = k_{15} \Big[HCOOH \Big] \Big[e^- \Big] - k_{16} \Big[H_3O^+ \Big] \Big[OH - HC^* - O^- \Big] = 0$$
$$\Rightarrow k_{15} \Big[HCOOH \Big] \Big[e^- \Big] = k_{16} \Big[H_3O^+ \Big] \Big[OH - HC^* - O^- \Big] \qquad \text{Eq49}$$

(50) Apply assumption (c) into equation Eq38;

$$\frac{d}{dt}\left[OH - HC^* - OH\right] = k_{16}\left[H_3O^+\right]\left[OH - HC^* - O^-\right] - k_{17}\left[OH - HC^* - OH\right]\left[e^-\right] = 0$$

$$\Rightarrow k_{16} \left[H_3 O^+ \right] \left[OH - HC^* - O^- \right] = k_{17} \left[OH - HC^* - OH \right] \left[e^- \right]$$
Eq50

(51) Apply assumption (c) into equation Eq39;

$$\frac{d}{dt} \Big[OH - C^{*(-)}H - OH \Big] = k_{17} \Big[OH - HC^* - OH \Big] \Big[e^- \Big] - k_{18} \Big[H_3 O^+ \Big] \Big[OH - C^{*(-)}H - OH \Big] = 0$$

$$\Rightarrow k_{17} \Big[OH - HC^* - OH \Big] \Big[e^- \Big] = k_{18} \Big[H_3 O^+ \Big] \Big[OH - C^{*(-)}H - OH \Big] \qquad \text{Eq51}$$

(52) Apply assumption (c) into equation Eq40;

$$\frac{d}{dt} [OH - CH_2 - OH] = k_{18} [H_3 O^+] [OH - C^{*(-)}H - OH] - k_{19} [OH - CH_2 - OH] = 0$$
$$\Rightarrow k_{18} [H_3 O^+] [OH - C^{*(-)}H - OH] = k_{19} [OH - CH_2 - OH]$$
Eq52

(53) Apply assumption (c) into equation Eq41;

$$\frac{d}{dt} \Big[HC^*H - O^- \Big] = k_{20} \Big[e^- \Big] \Big[HCHO \Big] - k_{21} \Big[H_3O^+ \Big] \Big[HC^*H - O^- \Big] = 0$$
$$\Rightarrow k_{20} \Big[e^- \Big] \Big[HCHO \Big] = k_{21} \Big[H_3O^+ \Big] \Big[HC^*H - O^- \Big]$$
Eq53

(54) Apply assumption (c) into equation Eq42;

$$\frac{d}{dt} \Big[HC^*H - OH \Big] = k_{21} \Big[H_3O^+ \Big] \Big[HC^*H - O^- \Big] - k_{22} \Big[HC^*H - OH \Big] \Big[H^* \Big] = 0$$
$$\Rightarrow k_{21} \Big[H_3O^+ \Big] \Big[HC^*H - O^- \Big] = k_{22} \Big[HC^*H - OH \Big] \Big[H^* \Big] \qquad \text{Eq54}$$

(55) Apply assumption (c) into equation Eq43:

$$\frac{d}{dt} \begin{bmatrix} C^* H_3 \end{bmatrix} = k_{23} \begin{bmatrix} H^* \end{bmatrix} \begin{bmatrix} CH_3 OH \end{bmatrix} - k_{24} \begin{bmatrix} C^* H_3 \end{bmatrix} \begin{bmatrix} H^* \end{bmatrix} = 0$$
$$\Rightarrow k_{23} \begin{bmatrix} H^* \end{bmatrix} \begin{bmatrix} CH_3 OH \end{bmatrix} = k_{24} \begin{bmatrix} C^* H_3 \end{bmatrix} \begin{bmatrix} H^* \end{bmatrix}$$
Eq55

(56) Apply assumption (a), (c) and (e) into equation Eq34

$$\frac{d}{dt} \Big[H_3 O^+ \Big] = k_3 \Big[H_2 O^+ \Big] \Big[H_2 O \Big] - k_{10} \Big[H_3 O^+ \Big] \Big[e^- \Big] \\ - k_{13} \Big[H_3 O^+ \Big] \Big[O = C^* - O^- \Big] - k_{16} \Big[H_3 O^+ \Big] \Big[OH - HC^* - O^- \Big] \\ - k_{18} \Big[H_3 O^+ \Big] \Big[OH - C^{*(-)} H - OH \Big] - k_{21} \Big[H_3 O^+ \Big] \Big[HC^* H - O^- \Big] = 0$$
Eq56-a

Substitute equation Eq46, Eq47, Eq49, Eq50, Eq51 and Eq53 into equation Eq56-a above and obtain:

$$k_{10} \Big[H_3 O^+ \Big] \Big[e^- \Big] = k_1 V \Big[H_2 O \Big] - k_{12} \Big[e^- \Big] \Big[CO_2 \Big] - 2k_{15} \Big[HCOOH \Big] \Big[e^- \Big] - k_{20} \Big[e^- \Big] \Big[HCHO \Big]$$
Eq56

(57) Apply assumption (c) into equation Eq44

$$\frac{d}{dt} [H_2 O_2] = k_4 [OH^*]^2 - k_6 [e^-] [H_2 O_2] = 0$$
$$\Rightarrow k_4 [OH^*]^2 = k_6 [e^-] [H_2 O_2]$$
Eq57

(58) Apply assumption (c) into equation Eq45

$$\frac{d}{dt} \begin{bmatrix} OH^* \end{bmatrix} = k_2 V \begin{bmatrix} H_2 O \end{bmatrix} + k_3 \begin{bmatrix} H_2 O^+ \end{bmatrix} \begin{bmatrix} H_2 O \end{bmatrix} - k_4 \begin{bmatrix} OH^* \end{bmatrix}^2$$

$$-k_5 \begin{bmatrix} OH^* \end{bmatrix} \begin{bmatrix} H^* \end{bmatrix} + k_6 \begin{bmatrix} e^- \end{bmatrix} \begin{bmatrix} H_2 O_2 \end{bmatrix} = 0$$

Eq58-a

Substitute equation Eq46 and Eq57 into equation Eq58-a above and obtain:

$$\left[OH^*\right] = \frac{k_2 V \left[H_2 O\right] + k_1 V \left[H_2 O\right]}{k_5 \left[H^*\right]}$$
Eq58

(59) Apply assumption (b) into equation Eq31

$$\frac{d}{dt} \Big[e^{-} \Big] = 2k_1 V \Big[H_2 O \Big] + k_2 V \Big[H_2 O \Big] - k_6 \Big[e^{-} \Big] \Big[H_2 O_2 \Big] - k_{10} \Big[H_3 O^{+} \Big] \Big[e^{-} \Big] - k_{12} \Big[CO_2 \Big] \Big[e^{-} \Big] \\ - k_{15} \Big[HCOOH \Big] \Big[e^{-} \Big] - k_{17} \Big[OH - HC^* - OH \Big] \Big[e^{-} \Big] - k_{20} \Big[e^{-} \Big] \Big[HCHO \Big] = 0$$
Eq59-a

Substitute equation Eq49, Eq50, Eq56, Eq57 and Eq58 into equation Eq59-a above and obtain:

$$\left[H^{*}\right] = \frac{\sqrt{k_{4}(k_{2}+k_{1})V[H_{2}O]}}{k_{5}}$$
 Eq59

(60) Apply assumption (f) into equation Eq25

$$\frac{d}{dt} [CO_2] = -k_{12} \Big[e^- \Big] [CO_2]$$
 Eq60-a

Substitute equation Eq46 into equation Eq60-a above and obtain:

$$\frac{d}{dt} \left[CO_2 \right] = -k_{12} \frac{k_1 V}{k_3} \left[CO_2 \right]$$
Eq60

(61) Substitute equation Eq59 into equation Eq26 and obtain:

$$\frac{d}{dt} [H_2] = k_{11} \frac{k_4 (k_2 + k_1) V [H_2 O]}{k_5^2}$$
Eq61

(62) Substitute equation Eq46, Eq47 and Eq48 into equation Eq27 and obtain:

$$\frac{d}{dt}[HCOOH] = \frac{k_1 V}{k_3} \left(k_{12} [CO_2] - k_{15} [HCOOH] \right)$$
Eq62

(63) Substitute equation Eq46 and Eq49 through Eq52 into equation Eq28 and obtain:

$$\frac{d}{dt}[HCHO] = \frac{k_1 V}{k_3} \left(k_{15} [HCOOH] - k_{20} [HCHO] \right)$$
Eq63

(64) Substitute equation Eq46, Eq53, Eq54 and Eq59 into equation Eq29 and obtain:

$$\frac{d}{dt} [CH_3OH] = k_{20} \frac{k_1 V}{k_3} [HCHO] - k_{23} \frac{\sqrt{k_4 (k_2 + k_1) V [H_2O]}}{k_5} [CH_3OH]$$
Eq64

(65) Substitute equation Eq55 and Eq59 into equation Eq30 and obtain:

$$\left|\frac{d}{dt}[CH_4] = k_{23} \frac{\sqrt{k_4(k_2 + k_1)V[H_2O]}}{k_5}[CH_3OH]\right|$$
Eq65

2. Reactions with Ionic Liquid as Solvent

A. Summary of Mechanism of Reactions

The mechanism of reactions with ionic liquid as solvent is the same with that with DI-water as solvent in Step 1 and 2, but they are different in Step 3.

Step 3: The following reactions will take place in the bulk of the fluid, all involving electron transfer. First, hydronium ion (H_3O^+) and electron (e^-) react to produce hydrogen radical (H^*) and water (H_2O) . Subsequently, two hydrogen radicals (H^*) combine to yield hydrogen molecules (H_2) as shown in Eq10 and Eq11. Next, CO₂ is reduced to yield CO₂ anion radicals $(CO_2^* \neg)$ which is shown in Eq12. Then, difference is shown up: CO₂ anion radicals react with BMIM-BF₄ to form the intermediate CO₂-BMIM-BF₄, which then reacts with hydronium ion (H_3O^+) to release BMIM-BF₄ and yield formate radical as shown below in Eq66 and Eq67. Formate radical combines with hydrogen radical to generate formic acid (HCOOH), as shown in Eq14. Afterwards, as the same as the first mechanism, the series of the reaction involving electron, hydronium ion and hydrogen radical lead to the formation of formaldehyde (HCHO), methanol (CH_3OH) and methane (CH_4) as shown from Eq15 to Eq24 in the first mechanism.



Eq66



Eq67

B. Differential Equations

Most of the differential equations for reactions in water are still working here except Eq34, Eq35 and Eq36, which will be changed to Eq68, Eq69 and Eq70 below. Besides, one more equation, Eq71, is added to represent the intermediate CO_2 -BMIM-BF₄.

(68) Concentration of hydronium ion, H_3O^+

$$\frac{d}{dt} \Big[H_3 O^+ \Big] = k_3 \Big[H_2 O^+ \Big] \Big[H_2 O \Big] - k_7 \Big[H_3 O^+ \Big] \Big[OH^- \Big] - k_{10} \Big[H_3 O^+ \Big] \Big[e^- \Big] \\ - k_{67} \Big[H_3 O^+ \Big] \Big[CO_2 - BMIM - BF_4 \Big] - k_{16} \Big[H_3 O^+ \Big] \Big[OH - HC^* - O^- \Big] \\ - k_{18} \Big[H_3 O^+ \Big] \Big[OH - C^{*(-)} H - OH \Big] - k_{21} \Big[H_3 O^+ \Big] \Big[HC^* H - O^- \Big]$$

(69) Concentration of $O = C^* - O^-$

$$\frac{d}{dt} \Big[O = C^* - O^- \Big] = k_{12} \Big[CO_2 \Big] \Big[e^- \Big] - k_{66} \Big[O = C^* - O^- \Big] \Big[BMIM - BF_4 \Big]$$
 Eq69

(70)Concentration of $O=C^*-OH$

$$\frac{d}{dt} \left[O = C^* - OH \right] = k_{67} \left[H_3 O^+ \right] \left[CO_2 - BMIM - BF_4 \right] - k_{14} \left[H^* \right] \left[O = C^* - OH \right]$$

Eq70

(71)Concentration of CO₂-BMIM-BF₄

$$\frac{d}{dt} [CO_2 - BMIM - BF_4] = k_{66} [O = C^* - O^-] [BMIM - BF_4] - k_{67} [H_3O^+] [CO_2 - BMIM - BF_4]$$
Eq71

C. Assumptions

Most the assumptions mentioned above still work here, except assumption (c) needs to add some content: the concentration of the intermediate CO_2 -BMIM-BF₄ is constant at Quasi-Steady-State

$$\frac{d}{dt} \left[CO_2 - BMIM - BF_4 \right] = 0$$

D. Simplifications of Differential Equations

Most simplified equations still work here, except several of them need to be modified, and some equations need to be added.

(72) Eq47 is changed by applying assumption (c) into equation Eq69

$$\frac{d}{dt} \Big[O = C^* - O^- \Big] = k_{12} \Big[CO_2 \Big] \Big[e^- \Big] - k_{66} \Big[O = C^* - O^- \Big] \Big[BMIM - BF_4 \Big] = 0$$

$$\Rightarrow k_{12} \Big[CO_2 \Big] \Big[e^- \Big] = k_{66} \Big[O = C^* - O^- \Big] \Big[BMIM - BF_4 \Big]$$
Eq72

(73) Apply assumption (c) into equation Eq71

$$\frac{d}{dt} [CO_2 - BMIM - BF_4] = k_{66} [O = C^* - O^-] [BMIM - BF_4] - k_{67} [H_3O^+] [CO_2 - BMIM - BF_4] = 0$$

$$\Rightarrow k_{66} [O = C^* - O^-] [BMIM - BF_4] = k_{67} [H_3O^+] [CO_2 - BMIM - BF_4] \qquad \text{Eq73}$$

(74) Eq48 is changed by applying assumption (c) into equation Eq70

$$\frac{d}{dt} \Big[O = C^* - OH \Big] = k_{67} \Big[H_3 O^+ \Big] \Big[CO_2 - BMIM - BF_4 \Big] - k_{14} \Big[H^* \Big] \Big[O = C^* - OH \Big] = 0$$
$$\Rightarrow k_{67} \Big[H_3 O^+ \Big] \Big[CO_2 - BMIM - BF_4 \Big] = k_{14} \Big[H^* \Big] \Big[O = C^* - OH \Big] \qquad \text{Eq74}$$

(75) Eq56-a is changed by applying assumption (a), (c) and (e) into equation Eq68

$$\frac{d}{dt} \Big[H_3 O^+ \Big] = k_3 \Big[H_2 O^+ \Big] \Big[H_2 O \Big] - k_7 \Big[H_3 O^+ \Big] \Big[OH^- \Big] - k_{10} \Big[H_3 O^+ \Big] \Big[e^- \Big] \\ - k_{67} \Big[H_3 O^+ \Big] \Big[CO_2 - BMIM - BF_4 \Big] - k_{16} \Big[H_3 O^+ \Big] \Big[OH - HC^* - O^- \Big] \\ - k_{18} \Big[H_3 O^+ \Big] \Big[OH - C^{*(-)}H - OH \Big] - k_{21} \Big[H_3 O^+ \Big] \Big[HC^* H - O^- \Big] = 0 \\ \text{Eq75}$$

Substitute equation Eq46, Eq49, Eq50, Eq51, Eq53, Eq72 and Eq73 into equation Eq75 above and still obtain Eq56.

Although the procedures are a little different, the results of these two mechanisms are the same.

3.2 Numerical Methods

3.2.1 COMSOL Multiphysics

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.⁴³

In this study, COMSOL Multiphysics is used to build a numerical model describing the performance of the microscale-based corona reactor for CO_2 reduction, and its extensive interface COMSOL-Matlab LiveLink is used to determine the reaction rate constants in this process.

3.2.2 Model Development

1. Defining Geometry

Since the width of the reactor is much larger than the thickness, the reactor can be assumed as parallel plates. A 2-D space dimension is chosen because there is no convection and diffusion in the direction along the width of the reactor. According to the size of the reactor, a rectangular with the height of 500µm and length of 22.4mm is built as shown in *Figure 13*. The height can be changed since different spacers will be used, but the length is fixed. The width of the reactor will be defined later in the Specifying Physics section.



Figure 13. Geometry of Corona Microreactor in COMSOL (Boundary 1: Inlet; Boundary 2,3: Wall; Boundary 4: Outlet)

B. Parameters

All the constants used to solve the model are defined here, including flow rate, outlet pressure, voltage applied on the reactor, initial concentration of CO₂, diffusion coefficients of CO₂ and all the products, and reasonable guesses of important reaction rate constants. The detailed table of parameters is shown in *Appendix B*.

C. Variables

All the intermediate variables required by the model are defined here, including reaction rates of CO_2 and all the products in the bulk and concentrations of hydrogen radical, electron and total carbon. The detailed table of variables is shown in *Appendix B*.

2. Physics Model

Two physics models are used in the numerical model: Laminar Flow model to simulate the velocity profile of the flow and Transport of Diluted Species model to simulate the concentration profiles of CO_2 and products.

The node properties setting in Laminar Flow model are shown below in *Table 3*.

	Compressibility	Incompressible flow						
	Turbulence Model Type	None						
Fluid	Density	From material						
Properties	Dynamic Viscosity	From material						
Wall ^a	Boundary Condition	No slip						
Initial Values ^b	Velocity Field, x	0 m/s						
	Velocity Field, y	0 m/s						
	Pressure	1 atm						
Inlet ^c	Boundary condition	Laminar inflow						
	Flow Rate	Defined in Parameters						
	Entrance Thickness ^d	1.06e-2 m						
	Entrance Length ^e	0.5 m						
Outlet ^f	Boundary condition	Pressure, no viscous						
		stress						
	Pressure	Defined in Parameters						

Table 3. Node Properties Setting in Laminar Flow Model

- a. Boundary 2,3 in *Figure 12* are defined as Wall.
- b. The initial values represent the situation before the fluid flows into the reactor.
- c. Boundary 1 in *Figure 12* is defined as Inlet.
- d. Entrance Thickness represents the width of the reactor as mentioned previously.
- e. Entrance Length is set to guarantee the fluid turns to laminar flow before it reaches the inlet of reactor.
- f. Boundary 4 in *Figure 12* is defined as Outlet.

The node properties setting in Transport of Diluted Species model are shown below in *Table 4*.

	Transport	Convection			
	Mechanisms				
	Dependent	6 species (CO_2 , $HCOOH$, $HCHO$, CH_3OH , CH_4 and			
	Variables	H ₂)			
Convection and	Diffusion	Defined in Parameters			
Diffusion	Coefficient				
No Flux ^a					
Initial Values ^b	Concentration	0 mol/m ³ for all species			
Reactions	Reactions	Defined in Variables			
Inflow ^c	Concentration	Except CO_2 defined in Parameters, all the others are 0 mol/m^3			
Outflow ^d					

Table 4. Node Properties Setting in Transport of Diluted Species Model

a. Boundary 2,3 in *Figure 12* are defined as No Flux.

- b. The initial values represent the situation before the fluid flows into the reactor.
- c. Boundary 1 in *Figure 12* is defined as Inflow.
- d. Boundary 4 in *Figure 12* is defined as Outflow.

3. Meshing

Since there is no dead spot in the geometry required to be specified, a mesh setting with maximum element size of 0.0437mm and minimum element size of 0.0201mm is satisfied for this model. The meshing of the geometry is shown below in *Figure 14*.



Figure 14. Meshing of the Geometry of Corona Microreactor

4. Solving and Visualizing Results

Make a horizontal cutline through middle of the reactor and study the velocity profile and concentration profiles, which are shown in *Figure 15* and *Figure 16* respectively.



Figure 15. Velocity Profile in the Corona Microreactor Produced in Numerical Model



Figure 16. Concentration Profiles in the Corona Microreactor Produced in Numerical Model

The velocity profile in *Figure 15* shows there is no disruption between the two parallel plates and is proved as laminar flow.

In the concentration profiles shown in *Figure 16*, CO_2 is always consumed so its profile goes all the way down along the reactor; intermediate products HCOOH, HCHO and CH₃OH are produced first and then consumed as new products are generated, therefore their profiles are shown as parabolic curves; final products CH₄ and H₂ are always produced so their profiles go all the way up through the reactor. The horizontally straight dash line represents the solubility of CO₂ in the solvent. Some tests on the numerical model are made (See Section 3.2.3).

3.2.3 Model Test

1. Setting No Voltage Applied on the Reactor

When there is no voltage applied on the reactor, there is no energy applied for the

reaction system, therefore, theoretically, there should be no reaction happening. That is to say, in the numerical model, reactant CO_2 should keep constant at the inlet concentration while the concentrations of all the products should remain at zero. *Figure 17* shows the result of the numerical model with no voltage applied, which agrees with the expectation.



Figure 17. Concentration Profiles in the Corona Microreactor Produced in Numerical Model When Voltage Applied on the Reactor V=0

2. Changing Flow Rate

Mean residence time and flow rate have the following relationship:

$$t_m = \frac{V_{volume}}{Q_V} = \frac{L \cdot W \cdot (2H)}{Q_V}$$

Where t_m is mean residence time; Q_V is flow rate; *L*, *W* and 2*H* are respectively the three dimensions of reactor. Therefore, the plot of Concentration vs. Length of the Reactor in *Figure 16* can be transferred into plot of Concentration vs. Mean Residence Time in *Figure 18*.



Figure 18. Plot of Concentration vs. Mean Residence Time in the Corona Microreactor

Then, flow rate is changed in the numerical model while the other parameters are fixed. When the flow rate is faster, the time the fluid stays in the reactor is shorter. Therefore, the conversion of CO_2 should be lower and lower with the increasing flow rate. For each flow rate, the ending concentrations have been recorded. *Figure 19 – 22* below show the results after changing flow rate. *Table 5* shows the ending concentrations of all six species for different flow rates (or different mean residence times).



Figure 19. Concentration Profile in the Corona Microreactor Produced in Numerical Model at Flow Rate Q = 8.5478 ml/hr



Figure 20. Concentration Profile in the Corona Microreactor Produced in Numerical Model at Flow Rate Q = 17.0957 ml/hr



Figure 21. Concentration Profile in the Corona Microreactor Produced in Numerical Model at Flow Rate Q = 42.7392 ml/hr



Figure 22. Concentration Profile in the Corona Microreactor Produced in Numerical Model at Flow Rate Q = 85.4784 ml/hr

Wodel										
Flow Rate (ml/hr)	Mean Residence Time (sec)	CO ₂ (mol/m ³)	HCOOH (mol/m ³)	HCHO (mol/m ³)	CH ₃ OH (mol/m ³)	CH ₄ (mol/m ³)	H ₂ (mol/m ³)			
4.2739	100	0.011	3.061E-05	2.623	9.875	21.537	57.320			
8.5478	50	0.625	1.726E-03	11.032	13.861	8.480	28.551			
17.0957	25	4.675	1.292E-02	18.256	8.973	2.104	14.171			
42.7392	10	15.527	4.297E-02	15.643	2.628	0.201	5.564			
85.4784	5	23.048	6.379E-02	10.126	0.794	0.025	2.724			

 Table 5. The Concentrations of All Species at the Outlet Produced by Numerical

 Model

Compare these results with those in *Figure 18*, they should match with each other. *Figure 23* shows the comparison result.



Figure 23. Comparison of the Concentration Profiles and the Results Produced by Changing Flow Rate

Figure 23 shows that the results by changing flow rate match with the concentration profiles, which agree with the expectation.

3.3 Higher Level Numerical Operations

In order 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 24* shows the scheme of this operation. First, initial guesses of reaction rate constants need to be offered for numerical model, and simulated results of concentrations are obtained. Then, these results and experimental data are used to calculate the initial objective function. Next, reaction rate constants are varied by using Matlab and a new objective function is calculated. If the absolute value of the error between initial and new objective function is smaller than the tolerance, then the reaction rate constants used for the new objective function would be the final results, otherwise, reaction rate constants will be repeatedly changed until it satisfies the requirement. A detailed procedure of this operation is shown in *Appendix C*.



Figure 24. Schematic of Numerical Model Optimization

Chapter 4- Experimental Set-up

4.1 Apparatus

The microscale-based corona reaction system in this study consists of the following components: syringe pump, microreactor, power supply, protection resistor and products collector. *Figure 25* and *26* are respectively schematic and photograph of this reaction system.



Figure 25. Schematic of Microscale-based Corona Reaction System



Figure 26. Photograph of Microscale-based Corona Reaction System

4.1.1 Syringe Pump

A Harvard Pump 33 Dual Syringe Pump, shown in *Figure 27*, is used to feed the reactant to the microreactor. It is really two pumps in one. Each side of this device has its own syringe rack, motor and lead screw. This pump has interfaces for computer control and data acquisition, which allows the pump to operate in a wider and more accurate range than the mechanical syringe pump. The syringe used to feed the reactant is a 25mL syringe with a removable luer lock from SGE Analytical Science.



Figure 27. Photograph of Harvard Pump 33 Dual Syringe Pump

4.1.2 Microreactor

The microscale-based corona reactor, as illustrated in *Figure 28-30*, consists of the following components: two stainless steel end plates, two Neoprene gaskets, two electrodes, one Teflon spacer and four stainless steel screws. Except the electrodes, all the other components are ordered from International Crystal Labs (Garfield, NJ). The descriptions of these components are shown below.

1. End plates

The two end plates can form a sealed liquid cell for spectrophotometer, but here these two stainless steel plates are used to ensure accurate visual alignment of the other components. There is a rectangular dispersive aperture on each of the plates, and there are two luer lock syringe filing ports on the front plate to use as inlet and outlet.

2. Gaskets

The dimensions of the Neoprene gaskets are 38.5mm \times 19.5mm \times 2mm. They are used to cushion and to form seals and insulations between the metal and electrodes.

3. Electrodes

Each electrode consists of three parts: one nickel plate, one graphite sheet and one L-shape nickel wire. A 99% nickel sheet with dimension of $12^{"} \times 2^{"} \times \frac{1}{2}^{"}$ is ordered from McMaster-Carr and is cut into nickel plates with the dimension of $39\text{mm} \times 19.5\text{mm} \times \frac{1}{2}^{"}$. They are used to support the graphite sheets. The reason why they are not directly used as electrodes is that nickel is corroded by the chemicals produced in the reaction system. The dimension of the graphite sheets is $39\text{mm} \times 19.5\text{mm} \times 0.2\mu\text{m}$. They are used as electrodes and directly contact with chemicals. The L-shape nickel wires are attached from the back side of nickel plates by using electrical tape. The function of the L-shape nickel wires is to connect the alligator clips which are linked to power supply and protection resistor.



Figure 28. Corona Microreactor Assembly (Exploded View)

4. Spacer

The dimensions of PTFE spacers are 38.5mm × 19.5mm and of different thicknesses (500µm or 200µm). The function of spacers is to create the channel space and form a seal between two electrodes.

5. Screws

Four stainless steel screws are used to assemble the microreactor system.



Figure 29. Corona Microreactor Components



Figure 30. Front View and Side View of Corona Microreactor
4.1.3 Power Supply

A Gibco Model 4001P Programmable Power Supply from Life Technologies, as illustrated in *Figure 31*, is used to provide electrical energy for the reaction system. A controlling program can be created to guarantee constant current and voltage supply. The voltage supply range of this device is 10V - 4000V.



Figure 31. Photograph of Gibco Model 4001P Programmable Power Supply

4.1.4 Protection Resistor

In order to prevent the power supply and microreactor from shorting that may occur, a protection resistor, as illustrated in *Figure 32*, is used in the circuit. It consists of two components: six 100k Ω MP925 Power Film Resistors and one breadboard. Two sets of three 100k Ω resistors in series are wired in parallel to form a 150k Ω resistor.



Figure 32. Photograph of Protection Resistor

4.1.5 Products Collector

A 50mL syringe with a removable luer lock from SGE Analytical Science is used as the products collector. The luer lock on the syringe can provide a better seal between outlet of microreactor and the collector to prevent from leaking.

4.1.6 Connection

Except the major components described above, the components used to link the system is also indispensable. The connection, as illustrated in *Figure 33*, consists of the following components: HPLC PEEK tubing (1/16" OD, 0.02" ID) from Supelco-Sigma Aldrich, ¹/₄-28 flangeless Delrin nuts, flangeless ETFE ferrules, PEEK female to male luer and PEEK female to female luer. The last four components are from Upchurch Scientific.



Figure 33. Photograph of Connection Components

4.1.7 Pressure Vessel

Because the high viscosity of ionic liquid influences the mass transfer of CO_2 , saturation of CO_2 in ionic liquid at atmosphere pressure cannot satisfy the requirement. A pressure vessel, as shown in *Figure 34*, is built to increase the partial pressure of CO_2 . It consists of five components: a type 304 stainless steel pipe with NPT of 1-1/2 and length of 4", two type 304 stainless steel caps with NPT of 1-1/2, a dual scale

pressure gauge (60 psi) with a dial size of 1-1/2" and a NPT 1/8 bottom connection, a 50 psi brass pressure release with a NPT 1/4 connection, and a stainless steel male connector and plug with a NPT of 1/8.



Figure 34. Photograph of Pressure Vessel

4.2 Operation Procedure

4.2.1 Saturation of CO₂ in Water and Ionic Liquid

Before the experiments, CO_2 gas needs to be dissolved into the solvent (water or ionic liquid). For saturation of CO_2 in water, a SodaStream soda maker was used for preparing the saturated CO_2 aqueous solution. A 1L pressure resistant bottle was filled with enough DI-water and connected to the soda maker. CO_2 gas was flown into the DI-water by pressing the button on the top of soda maker and DI-water was saturated when hearing 3 buzzes. For saturation of CO_2 in ionic liquid, the pressure vessel, as shown in *Figure 33*, is used for preparing the saturated CO_2 ionic liquid solution. 50mL ionic liquid was filled into the pressure vessel, which is then connected to CO_2 gas tank. The valve on the gas tank was turned on and outlet pressure was set at 20 psi. Ionic liquid was saturated after flowing for 10 minutes.

4.2.2 Start Procedure

The following procedure outlines the reactor start up for each experiment. First, the solution was filled into syringe (25mL for aqueous solution, and 10mL for ionic liquid solution because of its high viscosity), which was then fixed on the syringe pump and connected to the system via luer lock. Flow rate and direction were set up on syringe pump according to mean residence time, and then turn on the syringe pump. After the first drop of reactant appeared from the outlet, power supply was turned on and applied voltage was set up. Usually, 10 minutes after the voltage was stable, product was generated in the reactor and appeared at the outlet. At this time, the collector (50mL syringe) was connected to the system via luer lock.

4.2.3 Experimental Conditions

The reactions were performed using saturated CO_2 solution (aqueous or Ionic Liquid solution) at the room temperature. The length and width of the microreactor were fixed, but the thickness of the spacer can be changed (200µm or 500µm). The flow rate can also be varied corresponding different mean residence time (5sec, 10sec, 25sec, 50sec, and 100sec). The voltage applied on the reactor was another parameter (20V or 22.5V, will be explained in detail in Section 5.3.1). The experimental conditions for CO_2 reduction are shown in *Table 6*.

Solvent	Thickness of Spacer (μm)	Voltage Applied on Reactor (V)	Mean Residence Time (sec)
DI-water	500	20	5, 10, 25, 50, 100
	500	22.5	5, 10, 25, 50, 100
	200	20	5, 10, 25, 50, 100
Ionic Liquid	500	20	5, 10, 25, 50, 100
	500	22.5	5, 10, 25, 50, 100
	200	20	5, 10, 25, 50, 100

Table 6. Experimental Conditions for Corona Discharge Reduction of CO₂

4.2.4 Shutdown Procedure

At the end of experiment, the reactor system was shut down by the following procedure. First, the syringe pump was turned off. Then, the collector was disconnected from the system. The products will be collected in different ways depending on different species needs to be measured: for CO_2 in ionic liquid solution, CH_3OH , HCHO and HCOOH, products can be filled into a 1.5mL vial; for CO_2 in aqueous solution, products need to be added excessive KOH solution first; for CH_4 and H_2 , products will be kept in the syringe with a gastight valve on the outlet. Finally, after collecting the products, the power supply was turned off.

4.3 Safety

From the chemical view, none of the chemicals used and produced in this reaction system are extremely toxic. Besides, due to the use of microtechnology, only a small amount of chemicals are consumed and generated. The pressure and temperature of this reaction system are not high, and there is no leaking problem during the operation procedure. From electrical view, due to the use of protection resistor, the voltage applied on the reactor is not high. The corona discharges cannot be seen from the outside when the reaction occurs. Furthermore, all the electrical wires used in this reaction system are covered with insulations. Above all, the safety of this reaction system can be guaranteed in both chemical and electrical perspective.

Chapter 5- Materials, Methods and Measurements

5.1 Materials

Carbon dioxide gas tank is ordered from the BOC Group, Inc., Murray Hill, NJ. Formic acid (91.5%, J. T. Baker, Center Valley, PA), formaldehyde (36.5% - 38%, Mallinckrodt Chemicals, Phillipsburg, NJ), methanol (HPLC grade, >99.9%, EMD Chemicals, Darmstadt, Germany), methane (100ppm analytical standard in nitrogen, Supelco Analytical, Bellefonte, PA), hydrogen (100ppm analytical standard in helium, Supelco Analytical, Bellefonte, PA) and potassium carbonate (Anhydrous, >99.0%, EMD Chemicals, Darmstadt, Germany) are used for making the calibration curves. Methylene blue (J. T. Baker, Center Valley, PA) and sodium bicarbonate (Baking Soda, 99%, Arm & Hammer, Princeton, NJ) are used for validation of reactor. Potassium hydroxide (Pellets, 88%, Macron Chemicals, Center Valley, PA) is used to extract carbonate anion and formate anion from the products for Ion Chromatography measurement. The ionic liquid used as solvent in this study is 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄, BASF quality, ≥98%, Sigma Aldrich, St. Louis, MO). DI-water (HPLC grade, Macron Fine Chemicals, Center Valley, PA) is used for experiment and analytical measurement.

5.2 Analytical Methods

5.2.1 Automatic Potentiometric Titrator

The technology of acid-base titration is used for reduction of sodium bicarbonate which is a significant experiment for validation of reactor. An automatic potentiometric titrator, as illustrated in *Figure 35*, is used in this study.

The concentrations of sodium bicarbonate in both the inlet and outlet are determined by measuring the volume of standard acid solution added into the sample. The standard acid used in this study is $0.02N H_2SO_4$. The pH values of the samples are around 8.3, where HCO₃⁻ dominates in the solution, and it is the starting point for titration. When the pH value reaches about 4.3, H_2CO_3 starts to dominate in the solution, and it is the ending point for titration. *Figure 36* shows the trend of carbonate titration.

The calibration curve for Sodium Bicarbonate is shown in *Figure 37*, and the analysis of the calibration data is in *Appendix D*.



Figure 35. Photograph of Automatic Potentiometric Titrator



Figure 36. Trend of Carbonate Titration



Figure 37. Calibration Curve for NaHCO₃ with Trend Line and Error Bars

5.2.2 Gas Chromatography (GC)

The technology of gas chromatography is used for detection of methanol, formaldehyde, methane and hydrogen from products. A SRI Model 8610C Gas Chromatography system, as illustrated in *Figure 38*, is used in this study.



Figure 38. Photograph of SRI Model 8610C Gas Chromatography System

The concentrations of methanol, formaldehyde, methane and hydrogen are determined

by measuring the peak areas of these three species on the chromatograph chart. The device used for detecting methanol, formaldehyde and methane is installed with a Flame Ionization Detector (FID) and a 2m length \times 2mm ID Porapak QS column, while the one for hydrogen detection is installed with a Thermal Conductivity Detector (TCD) and same column. The operation conditions of the measurement are: 1µL injection volume for liquid sample and 1mL for gas sample, column temperature starting 70°C and ramping at 15°C/min until reaching 240°C, N₂ used as carrier gas with inlet pressure at 38psi, the FID hydrogen was set at 40psi, and the air flow was set at 40psi. In this condition, the peaks of methanol, formaldehyde, methane and hydrogen show at the range of 3.5 – 4.5 minutes, 7.5 – 8.15 minutes, 0.30 – 0.40 minutes and 0.35-0.5 minutes respectively.

Methanol and formaldehyde can be detected using external calibration, and the calibration curves for these two species are shown in *Figure 39* and *40*, and the analysis of the calibration data is in *Appendix D*.

Methane and hydrogen can also be detected using external calibration, either, but some modifications need to be made. Since there is only pure methane (and hydrogen) and 100ppm methane (and hydrogen) sold in the market and it is hard to guarantee the quality of mixing gases to certain concentrations by ourselves. The method of changing injection volume is chosen, and each volume (0.1mL, 0.5mL, 1mL, 5mL, 10mL) correspond a certain concentration. Calibration curve is made by measuring the peak areas and setting the intercept as 0, which is shown in *Figure 41* and *42*, and the analysis of the calibration data is in *Appendix D*.



Figure 39. Calibration Curve for CH₃OH with Trend Line and Error Bars



Figure 40. Calibration Curve for HCHO with Trend Line and Error Bars



Figure 41. Calibration Curve for CH₄ with Trend Line and Error Bars



Figure 42. Calibration Curve for H_2 with Trend Line and Error Bars

5.2.3 Ion Chromatography (IC)

The technology of Ion Chromatography is used for detection of formic acid. A Dionex ICS-5000⁺ Reagent-Free HPIC system, as illustrated in *Figure 43*, is used in this study.



Figure 43. Photograph of Dionex ICS-5000⁺ Reagent-Free HPIC System

The concentrations of formic acid are determined by measuring the peak areas of formate anion on the chromatograph chart. The formate anion is extracted by flowing products into potassium hydroxide solution. The device consists of an autosampler (AS-AP), a detector/chromatography (DC) compartment, a dual pump (DP) and an eluent generator (EG). The operation conditions of the measurement are: 25μ L injection volume, temperatures of DC compartment and column keeping at 30° C, NaOH as eluent type and 1mM eluent concentration, and setting flow rate of dual pump at 1.5mL/min. In this condition, the peak of formate anion shows at the range of 6.8 - 8.5 minutes.

Formic acid can be detected using external calibration, and the calibration curve is shown in *Figure 44*, and the analysis of the calibration data is in *Appendix D*.



Figure 44. Calibration Curve for HCOOH with Trend Line and Error Bars

5.2.4 pH/Conductivity Meter

The conductivity meter is used for detection of CO_2 in the outlet stream. A Fisher Scientific AR20 Accumet pH/Conductivity Meter, as illustrated in *Figure 45*, is used in this study.

The concentration of CO_2 is determined by measuring the conductivity of potassium carbonate (K₂CO₃), which is produced by using potassium hydroxide (KOH) to extract CO₂. The detailed operation procedure is: (1) flow products into excessive KOH solution. In this way, only CO₂ and formic acid can be extracted, and only three species (K₂CO₃, KCOOH, and KOH) are electrical conductive; (2) concentration of KCOOH can be determined by using ion chromatography as mentioned above, and concentration of KOH can be determined by measuring pH of the solution; (3) using the calibration curves in *Figure 46* to calculate the conductivities of KCOOH and KOH in the solution; (4) measuring the total conductivity of the solution and subtract

the ones for KCOOH and KOH from it to obtain the conductivity of K_2CO_3 ; (5) using the calibration curve for K_2CO_3 in *Figure 46* to determine its concentration, which is equal to the concentration n of CO₂. The analysis of the calibration data is in *Appendix D*.



Figure 45. Photograph of Fisher Scientific AR20 Accumet pH/Conductivity Meter



Figure 46. Calibration Curves for KCOOH, KOH and K₂CO₃ with Trend Line and Error Bars

5.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

The technology of Fourier Transform Infrared Spectroscopy (FTIR) is used for detection of CO_2 in ionic liquid solution at the outlet stream. A Bruker Vertex 70 FT-IR spectrometer, as illustrated in *Figure 47*, is used in this study.

The concentration of CO_2 in ionic liquid solution is determined by measuring the peak height of carbon-oxygen double bond (wavenumber between 2300 cm⁻¹ and 2400 cm⁻¹) on the spectrogram. The calibration curve of CO_2 is shown in *Figure 48*. The analysis of the calibration data is shown in *Appendix D*.



Figure 47. Photograph of Bruker Vertex 70 FT-IR Spectrometer



Figure 48. Calibration Curves for CO₂ with Trend Line and Error Bars

5.3 Validation of Reactor

5.3.1 Voltage-Current Test

The voltage-current test includes certification of corona discharge, determination of the turn-on voltage (the voltage necessary to discharge the corona) and establishment of the relationship between the voltage drop across the reactor and voltage generated by the power supply. A Fluke Model 77 multimeter was used for the tests by placing its electrodes on the opposite sides of the reactor with saturated CO_2 aqueous solution flowing through the reaction volume and power supply turned on. *Figure 49* shows the voltage-current plot (I-V curve) for the whole system and a partial enlarged drawing at lower voltage.



Figure 49. Voltage-Current Plots for CO₂ Solutions at Different Concentrations and Partial Enlarged Drawing

This experiment displayed a consistent voltage-current plot for CO_2 solutions at different concentrations, which indicates the electrical energy instead of electrons was consumed in this process. Also, the voltage-current plot for pure water also proves that corona discharge was produced in this process because electrochemical system cannot show any result for pure water. These results certified that a positive corona microreactor system was successfully crafted and the designed circuit was closed between the two electrodes encasing the reaction volume.

Various voltage-current plots also displayed a turn-on voltage of approximately 18-20V to activate the corona reaction system. At this time, the current got saturated, so the voltage stayed at a relatively stable level. The dissociation process continued until the voltage suddenly dropped, which is called breakdown process. After that, the resistance of the reactor started to decrease so the voltage is stable again.

Due to the amount of power supplied to the reaction system, protection resistance was necessary in order to keep the circuit from shorting. However, the protection resistance created a vast difference between the voltage generated by the power supply and that applied across the reactor. *Figure 50* below shows the relationship of these two voltages.



Figure 50. Relationship of Voltage Generated by Power Supply and that Applied to the Reactor

As shown in *Figure 50*, the turn-on voltage was reached when the power supply produced about 100V voltage. The voltage on the reactor stayed around 20V before the voltage generated by the power supply reached 500V. A sudden drop of the voltage on the reactor happened at this voltage. After that, the growth of voltage generated by power supply cannot increase the voltage on the reactor any more due to the decrease of the resistance of the reactor. In this process, the maximum voltage applied to the reactor was found (22.5V) while the power supply provided 210V voltage for the circuit. Another voltage used for our study is 20V voltage on the reactor while 500V voltage was generated from the power supply.

5.3.2 Reduction of Methylene Blue

Reduction of aqueous methylene blue is the second validation experiment, which provided confidence that hardware development of the corona microreactor was on track. The reason to choose methylene blue is that the experimental results can be distinguishable by naked eyes since the blue color of methylene blue becomes clear as it is reduced in the solution. In this experiment, 20ppm methylene blue aqueous solution is flown into the reactor at the rate of 2.1370mL/hr (corresponding to mean residence time at 80 sec) with 500V voltage applied to the reactor and 200µm spacer used. *Figure 51* shows the result of reduction of methylene blue on the microscale-based corona reactor.



Figure 51. Result of Reduction of Methylene Blue

5.3.3 Reduction of Sodium Bicarbonate

Reduction of Sodium Bicarbonate is another validation experiment which is closer to the goal: reduction of CO_2 . The following equations⁴⁴ illustrate the relationship between the CO_2 and bicarbonate.

$$CO_{2} + H_{2}O \longleftrightarrow H_{2}CO_{3}$$
$$H_{2}CO_{3} \longleftrightarrow H^{+} + HCO_{3}^{-}$$

This validation experiment provided more confidence that the reactor was ready for CO_2 reduction. Since products of methylene blue reduction have no influence on the pH of the solution, the technology of acid-based titration is used to determine the concentrations of sodium bicarbonate in both the inlet and outlet. In this experiment, 300ppm sodium bicarbonate aqueous solution is flown into the reactor with 500V voltage applied to the reactor and 500µm spacer used. *Table 7* and *Figure 52* illustrate the results of this experiment.

Mean Residence Time (sec)	Concentration of Sodium Bicarbonate (ppm)	
0	300	
5	199.519	
25	150.584	
50	131.684	
75	123.024	
100	115.567	

 Table 7. Experimental Data of Reduction of Sodium Bicarbonate



Figure 52. Result of Reduction of Sodium Bicarbonate

5.3.4 Control Test for CO₂ Reduction

Two experiments were respectively run for both solutions (aqueous solution and ionic liquid solution) and the following observations were made:

- 1) With CO_2 saturated in water (or ionic liquid) and no electrical power applied on the reactor, the concentrations of CO_2 in the inlet and outlet streams were identical and no product was generated.
- 2) With DI-water (or ionic liquid) and 20V electrical power applied on the reactor, no carbon-based products was produced in the outlet stream, and hydrogen was generated because of the split of water.

These match with the prediction and confirm the performance of the corona microreactor.

Chapter 6- Experimental Data

6.1 Reduction of CO₂ in Aqueous Solution

The performance of the reactor is influenced by three factors including mean residence time, thickness of the spacer, and the voltage applied on the reactor. Three experiments were performed by changing these factors: 500 μ m spacer with 20V voltage applied on reactor, 500 μ m spacer with 22.5V voltage applied on the reactor and 200 μ m spacer with 20V voltage applied on the reactor. In each of the experiment, data at different mean residence time (0 sec, 5 sec, 10 sec, 25 sec, 50 sec and 100 sec) were collected. The results are shown in *Figure 53-55* and the comparisons of each species in these three conditions are shown in Figure 56-61. The experimental data will be shown in *Appendix E*.



Figure 53. Experimental Result (20V Voltage, 500µm Spacer, Aqueous Solution)



Figure 54. Experimental Result (22.5V Voltage, 500µm Spacer, Aqueous Solution)



Figure 55. Experimental Result (20V Voltage, 200µm Spacer, Aqueous Solution)



Figure 56. Comparison of CO₂ Data in Different Conditions (Aqueous Solution)



Figure 57. Comparison of HCOOH Data in Different Conditions (Aqueous Solution)



Figure 58. Comparison of HCHO Data in Different Conditions (Aqueous Solution)



Figure 59. Comparison of CH₃OH Data in Different Conditions (Aqueous Solution)



Figure 60. Comparison of CH₄ Data in Different Conditions (Aqueous Solution)



Figure 61. Comparison of H₂ Data in Different Conditions (Aqueous Solution)

6.2 Reduction of CO₂ in Ionic Liquid Solution

Similar as the experiments in aqueous solution, three experiments were performed in ionic liquid BMIM-BF₄ solution (with 5% water w/v) in three different conditions: 500 μ m spacer with 20V voltage applied on reactor, 500 μ m spacer with 22.5V voltage applied on the reactor and 200 μ m spacer with 20V voltage applied on the reactor. In each of the experiment, data at different mean residence time (0 sec, 5 sec, 10 sec, 25 sec, 50 sec and 100 sec) were collected. The results are shown in *Figure 62-64* and the comparisons of each species in these three conditions are shown in Figure 65-70. The experimental data will be shown in *Appendix E*.

There is a difference between experiments conducted in aqueous solution and ionic liquid BMIM-BF₄ solution: in aqueous solution, CO_2 was the limiting reagent; however, in ionic liquid BMIM-BF₄ solution, water limited the generation of products. In this study, water content in ionic liquid BMIM-BF₄ solution is 5% w/v, and from balance of hydrogen, one can conclude the water was almost consumed in the system, which explains why the plots, shown below in *Figure 62-64*, leveled off at the end.



Figure 62. Experimental Result (20V Voltage, 500µm Spacer, Ionic Liquid Solution) and Partial Enlarged Drawing



Figure 63. Experimental Result (22.5V Voltage, 500µm Spacer, Ionic Liquid Solution) and Partial Enlarged Drawing



Figure 64. Experimental Result (20V Voltage, 200µm Spacer, Ionic Liquid Solution) and Partial Enlarged Drawing



Figure 65. Comparison of CO₂ Data in Different Conditions (Ionic Liquid Solution)



Figure 66. Comparison of HCOOH Data in Different Conditions (Ionic Liquid Solution)



Figure 67. Comparison of HCHO Data in Different Conditions (Ionic Liquid Solution)



Figure 68. Comparison of CH₃OH Data in Different Conditions (Ionic Liquid Solution)



Figure 69. Comparison of CH₄ Data in Different Conditions (Ionic Liquid Solution)



Figure 70. Comparison of H₂ Data in Different Conditions (Ionic Liquid Solution)

Chapter 7- Experimental Results

7.1 Optimization of the Numerical Model

The code of optimization program for corona reactor was built as shown in *Appendix C*. The model prediction lines were generated from the model after the reaction rate constants were discovered, which are illustrated in *Figure 71-76* with comparison with experimental data. Reaction rate constants were obtained by fitting the mathematical model to experimental data (optimization process) generated from the corona reactor for the reduction of CO_2 in both aqueous solution and ionic liquid solution, as shown in *Table 8* and *Table 9*.



Figure 71. Comparison of Optimization Result and Experimental Data (20V Voltage, 500µm Spacer, Aqueous Solution)



Figure 72. Comparison of Optimization Result and Experimental Data (22.5V Voltage, 500µm Spacer, Aqueous Solution)



Figure 73. Comparison of Optimization Result and Experimental Data (20V Voltage, 200µm Spacer, Aqueous Solution)


Figure 74. Comparison of Optimization Result and Experimental Data (20V Voltage, 500µm Spacer, Ionic Liquid Solution) and Partial Enlarged Drawing



Figure 75. Comparison of Optimization Result and Experimental Data (22.5V Voltage, 500µm Spacer, Ionic Liquid Solution) and Partial Enlarged Drawing



Figure 76. Comparison of Optimization Result and Experimental Data (20V Voltage, 200µm Spacer, Ionic Liquid Solution) and Partial Enlarged Drawing

Reaction Rate Constants	20V, 500μm	22.5V, 500μm	20V, 200μm
Production Rate Constant of H ₂ [m ³ /(mol·s)], k ₁₁	3.04×10 ⁻²	3.02×10 ⁻²	3.14×10 ⁻²
Consumption Rate Constant of CO ₂ [m ³ /(mol·s)], k ₁₂	2.72×10 ⁻³	2.70×10 ⁻³	2.63×10 ⁻³
Production Rate Constant of HCHO [m ³ /(mol·s)], k ₁₅	9.82×10 ⁻¹	9.81×10 ⁻¹	9.80×10 ⁻¹
Production Rate Constant of CH ₃ OH [m ³ /(mol·s)], k ₂₀	9.80×10 ⁻⁴	9.81×10 ⁻⁴	9.77×10 ⁻⁴
Production Rate Constant of CH ₄ $[m^3/(mol \cdot s)], k_{23}$	4.78×10 ⁻³	4.80×10 ⁻³	5.02×10 ⁻³
Production Rate Constant of H* [1], $K=((k_1+k_2)\cdot k_4)^{0.5}/k_5$	3.31×10 ⁻³	3.30×10 ⁻³	3.30×10 ⁻³

Table 8. Optimization Results in Aqueous Solution

 Table 9. Optimization Results in Ionic Liquid Solution

Reaction Rate Constants	20V, 500µm	22.5V, 500μm	20V, 200μm
Production Rate Constant of H ₂ [m ³ /(mol·s)], k ₁₁	1.65×10 ⁻⁵	1.67×10 ⁻⁵	1.65×10 ⁻⁵
Consumption Rate Constant of $CO_2 [m^3/(mol \cdot s)], k_{12}$	6.40×10 ⁻³	6.41×10 ⁻³	6.53×10 ⁻³
Production Rate Constant of HCHO [m ³ /(mol·s)], k ₁₅	1.48×10^{0}	1.48×10^{0}	1.48×10^{0}
Production Rate Constant of CH ₃ OH [m ³ /(mol·s)], k ₂₀	8.40×10 ⁻⁴	8.38×10 ⁻⁴	8.47×10 ⁻⁴
Production Rate Constant of CH ₄ [m ³ /(mol·s)], k ₂₃	1.90×10 ⁻³	1.92×10 ⁻³	1.99×10 ⁻³
Production Rate Constant of H* [1], $K = ((k_1+k_2)\cdot k_4)^{0.5}/k_5$	2.19×10 ⁻²	2.16×10 ⁻²	2.17×10 ⁻²

7.2 Analysis of Results

From the experimental data for reduction of CO_2 in aqueous solution, several results can be easily noticed: 1) CO_2 was saturated (concentration 34.002mol/m³) in aqueous solution before the reactions began, and its concentration decreased along with the increasing mean residence time; 2) hardly any formic acid was detected at the outlet stream; 3) concentrations of intermediate compounds, formaldehyde and methanol, grew up first and then reduced; 4) concentrations of methane and hydrogen raised along with the increasing mean residence time; 5) balance of carbon element can be guaranteed at different mean residence time; 6) higher applied voltage on the reactor resulted in better performance; 7) thickness of spacer had little influence on the performance of the reactor.

From the experimental data for reduction of CO_2 in ionic liquid solution, similar results can be observed: 1) CO_2 was saturated (concentration 992.422mol/m³) in ionic liquid solution before the reactions began, and its concentration decreased along with the increasing mean residence time; 2) hardly any formic acid was detected at the outlet stream; 3) concentrations of intermediate compounds, formaldehyde and methanol, grew up first and then reduced; 4) concentrations of methane and hydrogen raised along with the increasing mean residence time, and much less hydrogen was produced than that in aqueous solution; 5) balance of carbon element can be guaranteed at different mean residence time; 6) higher applied voltage on the reactor resulted in better performance; 7) thickness of spacer had little influence on the performance of the reactor.

The conversion of CO_2 in aqueous solution can reach 80.0% - 81.9% at applied voltage of 20V, and even 94.8% at applied voltage of 22.5V (maximum voltage current power supply can produce). Although in ionic liquid solution the conversion of CO_2 is much lower (18.3 – 18.5% at applied voltage of 20V, and 19.3% at applied voltage of 22.5V), solubility of CO_2 in ionic liquid is almost 30 times larger than that in water and consumption of CO_2 in ionic liquid is 6 – 7 times larger than that in water when generating same volume of products.

For the optimization results, the optimization result fitted the experimental data pretty well. Six primary reaction rate constants were obtained in both solutions. Compare the rate constants in these two solutions, except the production rate constants of hydrogen and hydrogen radical, rate constants for the same reactions are in the same magnitude. The reason why the production rate constants of hydrogen and hydrogen radical have great variation is that the concentration of water in ionic liquid is low, which influence the formation of hydrogen radical and hydrogen. Also, rapid conversion of formic acid leads to large value for production rate constant of formaldehyde.

Chapter 8- Contribution to Science and Conclusions

8.1 Contribution to Science

This study contributes to science by creating a fundamental designed model for CO_2 reduction. This tool passed three fundamental tests (including global test, dynamic test and local test) by accomplishment of balance of carbon element, proper operation and safe start and shutdown procedure. It also makes a contribution to science by producing the experimental data for CO_2 reduction and calculating the reaction rate constants, which can be used to predict similar reactions under various conditions.

8.2 Conclusions

A model for the reduction of CO_2 in corona microreactor was built. The microreactor in the investigation utilized spacers with thicknesses of 500µm and 200µm. Different volumetric flow rates of carbon dioxide saturated solution (aqueous or ionic liquid solution) corresponding to different mean residence times were set in the range of 5 to 100 seconds. The power supply in the study applied voltages of 20V and 22.5V on the microreactor to offer powers with different intensities. The experiments were conducted at room temperature (around 25°C). Samples were collected and analyzed via various analytical methods, including GC, IC, FTIR and conductivity.

It was determined that electrical power plays a major role in the reduction of CO_2 and ionic liquid captures and reduces more CO_2 than DI-water. It was also observed that there is hardly any impact from thickness of spacer in the range from 200µm to 500µm and an increase of applied voltage on reactor results in better performance. Besides, experiments also show that the reduction reaction does not take place in the absence of electrical power or reactant, which confirms the reaction mechanism.

The concentration of CO_2 exiting the microreactor decreases as mean residence time increases. The intermediate compound, formic acid, was converted from CO_2 but turned into formaldehyde quickly, so there is little formic acid at the outlet of

microreactor. The other two intermediate compounds, formaldehyde and methanol, were produced and then consumed with the increase of mean residence time. The concentrations of methane and hydrogen, the final products, exiting the microreactor increases as mean residence time increases.

The mathematical model developed specifically to describe the microreactor operation was solved using COMSOL software. The model was fitted to experimental data by using COMSOL-Matlab LiveLink to predict the reaction rate constants. It was found that the optimization result explained the experimental data very well. We feel confident 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.

In summary, reduction of CO_2 can be achieved in a microreactor by feeding saturated CO_2 solution under corona discharge at room temperature. The mathematical models proposed, along with the corresponding numerical solutions obtained, were accurate enough to extract the reaction rate constants and to predict the concentration profiles of the reactant and products in the microreactor.

Chapter 9- Recommendations for Future Work

In this project, the ionic liquid BMIM-BF₄ was studied and approved as solvent for CO_2 reduction. Some other kinds of ionic liquid, like EMIM-BF₄, can also be used for this reaction. It would be interesting to compare these two solvents. Also, the ionic liquid BMIM-BF₄ solution used in this study contains small amount of water (5% w/v). It is possible that water content of ionic liquid influences the reaction, so ionic liquid solutions with different water content can be studied.

From the experimental data, it is easily noticed that the conversion of CO_2 in ionic liquid can still be enhanced. Increase of mean residence time will be helpful to reach this goal, and it can be done in two ways: increasing the length of reactor, and decreasing the flow rate.

Further into the research, industrial application should be discussed. The number-up strategy will be studied, which includes sending CO_2 solution stream through numerous microreactors in series and parallel and arrangement of the power source. The capacity will be enhanced due to the increasing volume of reactant and decreasing overall cost.

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Appendix

Appendix A. Calculation of Diffusion Coefficients

- For CO₂, CH₄ and H₂, The values of diffusion coefficients at infinite dilution in water at 25°C (298K) are found in Table 5.2-1 from E.L.Cussler's *Diffusion: Mass Transfer in Fluid System*⁴¹.
- 2. For HCOOH, HCHO and CH₃OH, the value of the diffusion coefficients in water at room temperature are calculated by using Wilke-Chang correlation:

$$D_{1-2} = \frac{7.4 \times 10^{-8} \left(\phi M_2\right)^{0.5} T}{\mu V_1^{0.6}}$$

Where molecular weight of solvent $M_2 = 18$ g/mol,

viscosity of solvent $\mu = 1$ cP,

absolute temperature T = 298K,

association factor for water $\phi = 2.6$ (dimensionless).

Species	Density of Solute ρ (g/cm ³)	Molecular Weight of Solute M ₁ (g/mol)	Molar Volume of Solute $V_I (\text{cm}^3/\text{mol}) = M_I / \rho$	Diffusion Coefficient D _{i-2} (m ² /sec)
нсоон	1.22	46	37.70	1.71×10 ⁻⁹
нсно	1.11	30	26.95	2.09×10 ⁻⁹
CH ₃ OH	0.79	32	40.46	1.64×10 ⁻⁹

Table A-1. Parameters for Wilke-Chang Correlation

3. For all the species in ionic liquid BMIM-BF₄, the value of the diffusion coefficients are calculated by using Stokes-Einstein equation:

$$D_{1-2} = \frac{k_B T}{6\pi\mu_2 r_1} \qquad r_1 = \left(\frac{3M_1}{4\pi\rho_1 N_A}\right)^{\frac{1}{2}}$$

Where Boltzmann's constant $k_B = 1.38 \times 10^{-23}$ J/K,

absolute temperature T = 298K,

viscosity of solvent $\mu_2 = 93.814 \text{cP}^{45}$,

Avagadro's Number $N_A = 6.02 \times 10^{23} \text{mol}^{-1}$.

Species	Molecular Radius for Solute r ₁ (Å)	Density of Solute ρ ₁ (g/cm ³)	Molecular Weight of Solute M ₁ (g/mol)	Diffusion Coefficient D _{i-2} (m ² /sec)
CO ₂	1.85	1.98×10 ⁻³	44	1.13×10 ⁻¹²
НСООН	2.47	1.22	46	9.44×10 ⁻¹²
НСНО	2.90	1.11	30	1.06×10 ⁻¹¹
СН ₃ ОН	2.53	0.79	32	9.22×10 ⁻¹²
CH ₄	1.42	6.60×10 ⁻⁴	16	1.09×10 ⁻¹²
H_2	1.39	9.00×10 ⁻⁵	2	1.13×10 ⁻¹²

Table A-2. Parameters for Stokes-Einstein Equation

The Diffusion Coefficients for these six species are shown below in *Table A-3*:

Species	$D_{i\text{-water}}(\mathrm{m}^2/\mathrm{sec})$	D _{i-BMIM-BF4} (m ² /sec)
CO ₂	1.92×10 ⁻⁹	1.13×10 ⁻¹²
CH ₄	1.49×10 ⁻⁹	9.44×10 ⁻¹²
\mathbf{H}_2	4.50×10 ⁻⁹	1.06×10 ⁻¹¹
нсоон	1.71×10 ⁻⁹	9.22×10 ⁻¹²
нсно	2.09×10 ⁻⁹	1.09×10 ⁻¹²
CH ₃ OH	1.64×10 ⁻⁹	1.13×10 ⁻¹²

Table A-3. Diffusion Coefficients

Table B-1. Input Parameters in Numerical Model with Water as Solvent			
Name	Value	Description	
flowrate	4.2739[ml/h]	Flow rate	
press	1[atm]	Outlet pressure	
V	27.936[mol/m^3]	Applied voltage on the reactor	
DCO2	1.92e-9[m^2/s]	Diffusion coefficient of CO ₂	
DHCOOH	1.72e-9[m^2/s]	Diffusion coefficient of HCOOH	
DHCHO	2.1e-9[m^2/s]	Diffusion coefficient of HCHO	
DCH3OH	1.65e-9[m^2/s]	Diffusion coefficient of CH ₃ OH	
DCH4	1.49e-9[m^2/s]	Diffusion coefficient of CH ₄	
DH2	4.5e-9[m^2/s]	Diffusion coefficient of H ₂	
cH2O	55555[mol/m^3]	Concentration of water	
c0CO2	34.09[mol/m^3]	Initial concentration of CO ₂	
k1_k3	1[1]	=k1/k3	
K	2.0763	=((k1+k2)*k4)^0.5/k5	
k11	3.7e-3[m^3/(mol*s)]	Rate constant of H ₂ production	
k12	1.4e-3[m^3/(mol*s)]	Rate constant of HCOOH production	
k15	0.5709[m^3/(mol*s)]	Rate constant of HCHO production	
k20	8.9842e-4[m^3/(mol*	(s)] Rate constant of CH ₃ OH production	
k23	1.6e-3[m^3/(mol*s)]	Rate constant of CH ₄ production	
Table B-2. In	put Parameters in Nu	merical Model with [BMIM][BF4] as Solvent	
Name	Value	Description	
flournata			
nowrate	4.2739[ml/h]	Flow rate	
press	4.2739[ml/h] 1[atm]	Flow rate Outlet pressure	
press V	4.2739[ml/h] 1[atm] 27.936[mol/m^3]	Flow rate Outlet pressure Applied voltage on the reactor	
press V DCO2	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s]	Flow rate Outlet pressure Applied voltage on the reactor Diffusion coefficient of CO ₂	
nowrate press V DCO2 DHCOOH	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO2Diffusion coefficient of HCOOH	
nowrate press V DCO2 DHCOOH DHCHO	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO2Diffusion coefficient of HCOOHDiffusion coefficient of HCHO	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO2Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH3OH	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH4	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO2Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH3OHDiffusion coefficient of CH3OH	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH4 DH2	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s] 1.13e-12[m^2/s]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO2Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH3OHDiffusion coefficient of CH4Diffusion coefficient of H2	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH4 DH2 cH2O	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s] 1.13e-12[m^2/s] 3300[mol/m^3]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO2Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH3OHDiffusion coefficient of CH4Diffusion coefficient of H2Concentration of water	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH4 DH2 cH2O cH2O c0CO2	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s] 1.13e-12[m^2/s] 3300[mol/m^3] 992.422[mol/m^3]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO2Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH3OHDiffusion coefficient of CH4Diffusion coefficient of H2Concentration of waterInitial concentration of CO2	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH4 DH2 cH2O cH2O c0CO2 k1_k3	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s] 1.13e-12[m^2/s] 3300[mol/m^3] 992.422[mol/m^3] 1[1]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO_2 Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH ₃ OHDiffusion coefficient of CH ₄ Diffusion coefficient of H2Concentration of waterInitial concentration of CO_2 $=k1/k3$	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH4 DH2 cH2O c0CO2 k1_k3 K	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s] 1.13e-12[m^2/s] 3300[mol/m^3] 992.422[mol/m^3] 1[1] 0.7[1]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO_2 Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH ₃ OHDiffusion coefficient of CH ₄ Diffusion coefficient of H2Concentration of waterInitial concentration of CO2=k1/k3=((k1+k2)*k4)^0.5/k5	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH4 DH2 cH2O cH2O c0CO2 k1_k3 K k11	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s] 1.13e-12[m^2/s] 3300[mol/m^3] 992.422[mol/m^3] 1[1] 0.7[1] 1.6e-2[m^3/(mol*s)]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO_2 Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH ₃ OHDiffusion coefficient of CH4Diffusion coefficient of H2Concentration of waterInitial concentration of CO2=k1/k3=((k1+k2)*k4)^0.5/k5Rate constant of H2 production	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH4 DH2 cH2O c0CO2 k1_k3 K k11 k12	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s] 1.13e-12[m^2/s] 3300[mol/m^3] 992.422[mol/m^3] 1[1] 0.7[1] 1.6e-2[m^3/(mol*s)] 6e-5[m^3/(mol*s)]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO_2 Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH ₃ OHDiffusion coefficient of CH ₄ Diffusion coefficient of H2Concentration of waterInitial concentration of CO2 $=k1/k3$ $=((k1+k2)*k4)^{0.5/k5}$ Rate constant of H2OOH production	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH4 DH2 cH2O c0CO2 k1_k3 K k11 k12 k15	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s] 1.13e-12[m^2/s] 3300[mol/m^3] 992.422[mol/m^3] 1[1] 0.7[1] 1.6e-2[m^3/(mol*s)] 6e-5[m^3/(mol*s)] 0.8[m^3/(mol*s)]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO_2 Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH ₃ OHDiffusion coefficient of CH4Diffusion coefficient of H2Concentration of waterInitial concentration of CO2=k1/k3=((k1+k2)*k4)^0.5/k5Rate constant of H2Rate constant of H2Rate constant of H2CONCENTRATIONRate constant of H2	
nowrate press V DCO2 DHCOOH DHCHO DCH3OH DCH3OH OCH3OH OCH3OH K k11 k12 k15 k20	4.2739[ml/h] 1[atm] 27.936[mol/m^3] 1.13e-12[m^2/s] 9.44e-12[m^2/s] 1.06e-11[m^2/s] 9.22e-12[m^2/s] 1.09e-12[m^2/s] 1.13e-12[m^2/s] 3300[mol/m^3] 992.422[mol/m^3] 1[1] 0.7[1] 1.6e-2[m^3/(mol*s)] 6e-5[m^3/(mol*s)] 9e-4[m^3/(mol*s)]	Flow rateOutlet pressureApplied voltage on the reactorDiffusion coefficient of CO_2 Diffusion coefficient of HCOOHDiffusion coefficient of HCHODiffusion coefficient of CH ₃ OHDiffusion coefficient of CH ₄ Diffusion coefficient of H2Concentration of waterInitial concentration of CO2=k1/k3=((k1+k2)*k4)^0.5/k5Rate constant of H2Rate constant of HCOOH productionRate constant of HCHO productionRate constant of CH3OH productionRate constant of CH3OH productionRate constant of CH3OH productionRate constant of CH3OH production	

Appendix B. Input Parameters and Variables in Numerical Model

Name	Expression	Unit	Description
cH_radical	K*(V*cH2O)^0.5	mol/m ³	Reaction rate of hydrogen radical production
cElectron	k1_k3*V	mol/m ³	Reaction rate of electron production
rCO2	-k12*cCO2*cElectron	$mol/(m^3 \cdot s)$	Reaction rate of CO ₂ consumption
rHCOOH	k12*cCO2*cElectron-k15*c HCOOH*cElectron	mol/(m ³ ·s)	Reaction rate of HCOOH production
rHCHO	k15*cHCOOH*cElectron-k2 0*cHCHO*cElectron	$mol/(m^3 \cdot s)$	Reaction rate of HCHO production
rCH3OH	k20*cHCHO*cElectron-k23 *cCH3OH*cH_radical	mol/(m ³ ·s)	Reaction rate of CH ₃ OH production
rCH4	k23*cCH3OH*cH_radical	$mol/(m^3 \cdot s)$	Reaction rate of CH ₄ production
rH2	k11*(cH_radical)^2	$mol/(m^3 \cdot s)$	Reaction rate of H ₂ production
C_balance	cCO2+cHCOOH+cHCHO+c CH3OH+cCH4	mol/m ³	Carbon balance

Table B-3. Input Variables in Numerical Model

Appendix C. Procedure of Optimization of Numerical Model

1. Save COMSOL model as a M-file

In the COMSOL desktop, go to "File" \rightarrow "Reset History" to release the history of previous programming. Then, go to "File" \rightarrow "Save As Model M-File", choose the directory and save it.

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, set model parameters, which would be the reaction rate constants. Next, at the end of this file, use the syntax *mphinterp* to extract data of concentration at certain position of the reactor and the syntax *mean* to calculate the average value along the vertical crossline. Finally, compute the objective function which is sum of squares of errors between experiment data and simulated results.

3. 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 reaction rate constants and set the options. Finally, run the major function and wait for the results.

The codes for the reaction in aqueous solution and ionic liquid solution are similar, so only the code for reaction in aqueous solution is shown here.

The code for the major function:

```
% fminsearch: find minimum of unconstrained multivarible function using
% derivative-free method
clear all, format compact
global k0
```

% Starting point k0 = [2.76*10^(-2) 1.4*10^(-3) 3.0496 8*10^(-4) 5.3*10^(-3) 3*10^(-3)]; % Options setting options = optimset('Display','iter','TolFun',0.1,'PlotFcns',@optimplotfval);

% k = the reaction rate constant
% fval = value of objective function
% exitflag = describe the exit condition of fminsearch
[k,fval,exitflag,output] = fminsearch('CO2Corona',k0,options);

The M-file used as objective function:

function f = CO2Corona(k)
%
% CO2Corona.m
%
% Model exported on Apr 2 2013, 12:55 by COMSOL 4.3.0.233.

import com.comsol.model.*
import com.comsol.model.util.*

model = ModelUtil.create('Model');

model.modelPath('I:\Thesis\COMSOL');

model.name('CO2_corona.mph');

% Set Model parameter k11,k12,k15,k20,k23,K

k1 = k(1); k2 = k(2); k3 = k(3); k4 = k(4); k5 = k(5);k6 = k(6);

figure(1),plot(k1,'o') hold on figure(2),plot(k2,'s') hold on figure(3),plot(k3,'d') hold on figure(4),plot(k4,'+') hold on figure(5),plot(k5,'v') hold on

```
figure(6),plot(k6,'x')
hold on
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
if k6<0,
     k6 = abs(k6);
end
model.param.set('k11',k1);
model.param.set('k12',k2);
model.param.set('k15',k3);
```

model.param.set('k15',k3); model.param.set('k20',k4); model.param.set('k23',k5); model.param.set('K',k6);

```
model.param.set('flowrate', '4.2739[ml/h]', 'flowrate');
model.param.set('press', '1[atm]', 'pressure outlet');
model.param.set('V', '31.428[mol/m^3]', 'appiled voltage');
model.param.set('coCo2', '34.09[mol/m^3]', 'initial concentration');
model.param.set('DCO2', '1.92e-9[m^2/s]', 'diff coef of CO2');
model.param.set('DHCOOH', '1.72e-9[m^2/s]', 'diff coef of HCOOH');
model.param.set('DHCHO', '2.1e-9[m^2/s]', 'diff coef of HCHO');
model.param.set('DCH3OH', '1.65e-9[m^2/s]', 'diff coef of CH3OH');
```

model.param.set('DCH4', '1.49e-9[m^2/s]', 'diff coef of CH4'); model.param.set('DH2', '4.5e-9[m^2/s]', 'diff coef of H2'); model.param.set('cH2O', '55555[mol/m^3]', 'concentrition of water'); %model.param.set('k11', '2.76e-2[m^3/(mol*s)]'); %model.param.set('k12', '1.4e-3[m^3/(mol*s)]'); %model.param.set('k15', '3.0496[m^3/(mol*s)]'); %model.param.set('k20', '8e-4[m^3/(mol*s)]'); %model.param.set('k23', '5.3e-3[m^3/(mol*s)]'); %model.param.set('K1', '3e-3[1]', '=((k1+k2)*k4)^0.5/k5'); model.param.set('k1_k3', '1[1]', '=k1/k3');

model.modelNode.create('mod1');

model.geom.create('geom1', 2); model.geom('geom1').lengthUnit('mm'); model.geom('geom1').feature.create('r1', 'Rectangle'); model.geom('geom1').feature('r1').set('pos', {'0' '0'}); model.geom('geom1').feature('r1').set('size', {'22.4' '0.5'}); model.geom('geom1').run;

model.variable.create('var1'); model.variable('var1').model('mod1'); model.variable('var1').set('cH_radical', 'K*(V*cH2O)^0.5'); model.variable('var1').set('cElectron', 'k1_k3*V'); model.variable('var1').set('rCO2', '-k12*cCO2*cElectron'); model.variable('var1').set('rHCOOH', 'k12*cCO2*cElectron-k15*cHCOOH*cElectron'); model.variable('var1').set('rHCHO', 'k15*cHCOOH*cElectron-k20*cHCHO*cElectron'); model.variable('var1').set('rCH3OH', 'k20*cHCHO*cElectron-k23*cCH3OH*cH_radical'); model.variable('var1').set('rCH4', 'k23*cCH3OH*cH_radical'); model.variable('var1').set('rH2', 'k11*cH_radical^2'); model.variable('var1').set('rL2', 'k11*cH_radical^2');

model.material.create('mat1');

model.physics.create('spf', 'LaminarFlow', 'geom1'); model.physics('spf').feature.create('inl1', 'Inlet', 1); model.physics('spf').feature('inl1').selection.set([1]); model.physics('spf').feature('out1', 'Outlet', 1); model.physics(create('chds', 'DilutedSpecies', 'geom1'); model.physics('chds').field('concentration').field('cCO2'); model.physics('chds').field('concentration').component({'cCO2' 'cHCOOH' 'cHCHO' 'cCH3OH' 'cCH4' 'cH2'}); model.physics('chds').feature.create('reac1', 'Reactions', 2); model.physics('chds').feature('reac1').selection.set([1]); model.physics('chds').feature.create('in1', 'Inflow', 1); model.physics('chds').feature('in1').selection.set([1]); model.physics('chds').feature.create('out1', 'Outflow', 1); model.physics('chds').feature('out1').selection.set([4]);

model.mesh.create('mesh1', 'geom1'); model.mesh('mesh1').feature.create('size1', 'Size'); model.mesh('mesh1').feature('size1').selection.geom('geom1', 1); model.mesh('mesh1').feature('size1').selection.set([2 3]); model.mesh('mesh1').feature.create('ftri1', 'FreeTri'); model.mesh('mesh1').feature('ftri1').selection.geom('geom1', 2); model.mesh('mesh1').feature('ftri1').selection.set([1]); model.mesh('mesh1').feature('b11').selection.geom('geom1', 2); model.mesh('mesh1').feature('b11').selection.geom('geom1', 2); model.mesh('mesh1').feature('b11').selection.geom('geom1', 2); model.mesh('mesh1').feature('b11').selection.set([1]); model.mesh('mesh1').feature('b11').feature.create('b1p1', 'BndLayerProp'); model.mesh('mesh1').feature('b11').feature('b1p1').selection.set([2 3]); model.mesh('mesh1').feature.create('ftri2', 'FreeTri');

model.result.table.create('tb11', 'Table'); model.result.table.create('tb12', 'Table'); model.result.table.create('tb13', 'Table'); model.result.table.create('tb14', 'Table'); model.result.table.create('tb15', 'Table'); model.result.table.create('tb16', 'Table'); model.result.table.create('tb16', 'Table');

model.view('view1').axis.set('xmin', '4.952831745147705'); model.view('view1').axis.set('xmax', '11.977182388305664'); model.view('view1').axis.set('ymin', '-3.4630165100097656'); model.view('view1').axis.set('ymax', '1.5553169250488281');

model.material('mat1').name('Water'); model.material('mat1').propertyGroup('def').func.name('Functions'); model.material('mat1').propertyGroup('def').set('density', '1000'); model.material('mat1').propertyGroup('def').set('dynamicviscosity', '8.94e-4');

model.physics('spf').prop('CompressibilityProperty').set('Compressibility', 'Incompressible');

model.physics('spf').prop('PseudoTimeProperty').set('locCFL',

'1.3^min(niterCMP-1,9)+if(niterCMP>25,9*1.3^min(niterCMP-25,9),0)+if(niterCMP>50,90*1.3^min(niterCMP-5 0,9),0)');

model.physics('spf').feature('fp1').set('minput_velocity_src', 'root.mod1.u');

model.physics('spf').feature('init1').set('p', '1[atm]');

model.physics('spf').feature('inl1').set('BoundaryCondition', 'LaminarInflow');

model.physics('spf').feature('inl1').set('U0in', 'velocity');

model.physics('spf').feature('inl1').set('LaminarInflowOption', 'V0');

model.physics('spf').feature('inl1').set('Uav', 'velocity');

model.physics('spf').feature('inl1').set('V0', 'flowrate');

model.physics('spf').feature('inl1').set('Lentr', '0.01');

model.physics('spf').feature('inl1').set('Dzentr', '1.06e-2');

model.physics('spf').feature('out1').set('p0', 'press');

model.physics('chds').feature('cdm1').set('u_src', 'root.mod1.u');

model.physics('chds').feature('cdm1').set('DiffusionMaterialList', 'mat1');

model.physics('chds').feature('cdm1').set('minput_concentration_src', 'root.mod1.cCO2');

model.physics('chds').feature('cdm1').set('D_1', {'DHCOOH'; '0'; '0'; 'D', 'DHCOOH'; '0'; '0'; 'D', 'DHCOOH'););

model.physics('chds').feature('cdm1').set('D_2', {'DHCHO'; '0'; '0'; 'D', 'DHCHO'; '0'; '0'; '0'; 'DHCHO'});

model.physics('chds').feature('cdm1').set('D_3', {'DCH3OH'; '0'; '0'; '0CH3OH'; '0'; '0'; '0'; 'DCH3OH'});

model.physics('chds').feature('cdm1').set('D_4', {'DCH4'; '0'; '0'; '0'; 'DCH4'; '0'; '0'; 'DCH4'});

model.physics('chds').feature('cdm1').set('D_5', {'DH2'; '0'; '0'; '0'; 'DH2'; '0'; '0'; '0'; 'DH2'});

model.physics('chds').feature('cdm1').name('Convection and Diffusion');

model.physics('chds').feature('init1').set('cCO2', 'le-16');

model.physics('chds').feature('init1').set('cHCHO', '1e-16');

model.physics('chds').feature('init1').set('cCH3OH', '1e-16');

model.physics('chds').feature('init1').set('cCH4', '1e-16');

model.physics('chds').feature('init1').set('cH2', '1e-16');

model.physics('chds').feature('init1').set('cHCOOH', 'le-16');

model.physics('chds').feature('reac1').set('R', {'rCO2'; 'rHCOOH'; 'rHCHO'; 'rCH3OH'; 'rCH4'; 'rH2'});

```
model.physics('chds').feature('in1').set('c0', {'c0CO2'; '0'; '0'; '0'; '0'; '0'});
```

model.mesh('mesh1').feature('size').set('table', 'cfd');

model.mesh('mesh1').feature('size').set('hauto', 8);

model.mesh('mesh1').feature('size1').set('table', 'cfd');

model.mesh('mesh1').feature('size1').set('hauto', 6);

model.mesh('mesh1').feature('bl1').feature('blp1').set('blnlayers', '2');

model.mesh('mesh1').feature('bl1').feature('blp1').set('blhminfact', '5');

model.mesh('mesh1').run;

model.frame('material1').sorder(1);

model.result.table('tbl2').comments('Line Integration 1 (chds.tfluxx_cCO2)'); model.result.table('tbl2').comments('Line Integration 2 (chds.tfluxx_cCO2)'); model.result.table('tbl3').comments('Line Integration 3 (chds.tfluxx_cHCOOH)'); model.result.table('tbl4').comments('Line Integration 4 (chds.tfluxx_cHCHO)'); model.result.table('tbl5').comments('Line Integration 5 (chds.tfluxx_cCH3OH)'); model.result.table('tbl6').comments('Line Integration 6 (chds.tfluxx_cCH4)'); model.result.table('tbl6').comments('Line Integration 7 (chds.tfluxx_cCH4)');

model.study.create('std1');

model.study('std1').feature.create('stat', 'Stationary');

model.sol.create('sol1');

model.sol('sol1').study('std1'); model.sol('sol1').attach('std1'); model.sol('sol1').feature.create('st1', 'StudyStep'); model.sol('sol1').feature.create('v1', 'Variables'); model.sol('sol1').feature.create('s1', 'Stationary'); model.sol('sol1').feature('s1').feature.create('fc1', 'FullyCoupled'); model.sol('sol1').feature('s1').feature.create('d1', 'Direct'); model.sol('sol1').feature('s1').feature.remove('fcDef');

model.result.dataset.create('cln1', 'CutLine2D'); model.result.dataset.create('cln2', 'CutLine2D'); model.result.dataset.create('cln3', 'CutLine2D'); model.result.create('pg1', 'PlotGroup2D'); model.result('pg1').feature.create('surf1', 'Surface'); model.result.create('pg2', 'PlotGroup2D'); model.result('pg2').feature.create('con', 'Contour'); model.result.create('pg3', 'PlotGroup2D'); model.result('pg3').feature.create('surf1', 'Surface'); model.result.create('pg4', 'PlotGroup1D'); model.result('pg4').set('probetag', 'none'); model.result('pg4').feature.create('lngr5', 'LineGraph'); model.result('pg4').feature.create('lngr7', 'LineGraph'); model.result('pg4').feature.create('lngr8', 'LineGraph'); model.result('pg4').feature.create('lngr9', 'LineGraph'); model.result('pg4').feature.create('lngr10', 'LineGraph'); model.result('pg4').feature.create('lngr11', 'LineGraph'); model.result('pg4').feature.create('lngr12', 'LineGraph'); model.result.create('pg5', 'PlotGroup1D'); model.result('pg5').set('probetag', 'none'); model.result('pg5').feature.create('lngr1', 'LineGraph');

model.result.export.create('plot1', 'Plot'); model.result.export.create('plot2', 'Plot'); model.result.export.create('plot3', 'Plot'); model.result.export.create('plot4', 'Plot'); model.result.export.create('plot5', 'Plot');

```
model.sol('sol1').attach('std1');
```

model.sol('sol1').feature('st1').name('Compile Equations: Stationary'); model.sol('sol1').feature('st1').set('studystep', 'stat'); model.sol('sol1').feature('v1').set('control', 'stat'); model.sol('sol1').feature('v1').feature('mod1_cHCHO').set('variables', 'mod1_H2'); model.sol('sol1').feature('v1').feature('mod1_cCO2').set('variables', 'mod1_cDiuron'); model.sol('sol1').feature('v1').feature('mod1_cHCOOH').set('variables', 'mod1_cH2O2'); model.sol('sol1').feature('v1').feature('mod1_cCH3OH').set('variables', 'mod1_cDiuron4'); model.sol('sol1').feature('v1').feature('mod1_cCH4').set('variables', 'mod1_cDiuron5'); model.sol('sol1').feature('v1').feature('mod1_cH2').set('variables', 'mod1_cDiuron6'); model.sol('sol1').feature('s1').set('control', 'stat'); model.sol('sol1').feature('s1').set('stol', '0.001'); model.sol('sol1').feature('s1').feature('fc1').set('dtech', 'hnlin'); model.sol('sol1').feature('s1').feature('fc1').set('maxiter', '5000'); model.sol('sol1').feature('s1').feature('fc1').set('probesel', 'manual'); model.sol('sol1').feature('s1').feature('d1').set('linsolver', 'pardiso'); model.sol('sol1').runAll;

```
model.result.dataset('cln1').name('Centerline');
model.result.dataset('cln1').set('genpoints', {'0' '0.25'; '22.4' '0.25'});
model.result.dataset('cln2').name('Cross section');
model.result.dataset('cln2').set('genpoints', {'19' '0'; '19' '0.4'});
model.result.dataset('cln3').set('genpoints', {'0' '0.2'; '21' '0.2'});
model.result('pg1').name('Velocity (spf)');
model.result('pg1').set('frametype', 'spatial');
model.result('pg2').name('Pressure (spf)');
model.result('pg2').set('frametype', 'spatial');
model.result('pg2').feature('con').set('expr', 'p');
model.result('pg2').feature('con').set('unit', 'Pa');
model.result('pg2').feature('con').set('descr', 'Pressure');
model.result('pg2').feature('con').set('number', '40');
model.result('pg3').name('Concentration (chds)');
model.result('pg3').feature('surf1').set('expr', 'cDiuron');
model.result('pg3').feature('surf1').set('unit', ");
model.result('pg3').feature('surf1').set('descr', 'Concentration');
```

model.result('pg4').name('Concentration profile'); model.result('pg4').set('data', 'cln1'); model.result('pg4').set('title', 'Concentration Profile'); model.result('pg4').set('xlabel', 'Length of the Reactor (mm)'); model.result('pg4').set('xlabelactive', true); model.result('pg4').set('ylabel', 'Concentration (mol/m³)'); model.result('pg4').set('ylabelactive', true); model.result('pg4').set('titletype', 'manual'); model.result('pg4').feature('lngr5').name('CO2'); model.result('pg4').feature('lngr5').set('data', 'cln1'); model.result('pg4').feature('lngr5').set('expr', 'cCO2'); model.result('pg4').feature('lngr5').set('unit', 'mol/m^3'); model.result('pg4').feature('lngr5').set('descr', 'Concentration'); model.result('pg4').feature('lngr5').set('legend', true); model.result('pg4').feature('lngr5').set('legendmethod', 'manual'); model.result('pg4').feature('lngr5').set('legends', {'CO2'}); model.result('pg4').feature('lngr5').set('smooth', 'none'); model.result('pg4').feature('lngr7').name('HCOOH'); model.result('pg4').feature('lngr7').set('data', 'cln1'); model.result('pg4').feature('lngr7').set('expr', 'cHCOOH'); model.result('pg4').feature('lngr7').set('unit', 'mol/m^3'); model.result('pg4').feature('lngr7').set('descr', 'Concentration'); model.result('pg4').feature('lngr7').set('legend', true); model.result('pg4').feature('lngr7').set('legendmethod', 'manual'); model.result('pg4').feature('lngr7').set('legends', {'HCOOH'}); model.result('pg4').feature('lngr7').set('smooth', 'none'); model.result('pg4').feature('lngr8').name('HCHO'); model.result('pg4').feature('lngr8').set('data', 'cln1'); model.result('pg4').feature('lngr8').set('expr', 'cHCHO'); model.result('pg4').feature('lngr8').set('unit', 'mol/m^3'); model.result('pg4').feature('lngr8').set('descr', 'Concentration'); model.result('pg4').feature('lngr8').set('legend', true); model.result('pg4').feature('lngr8').set('legendmethod', 'manual'); model.result('pg4').feature('lngr8').set('legends', {'HCHO'}); model.result('pg4').feature('lngr8').set('smooth', 'none'); model.result('pg4').feature('lngr9').name('CH3OH'); model.result('pg4').feature('lngr9').set('data', 'cln1'); model.result('pg4').feature('lngr9').set('expr', 'cCH3OH'); model.result('pg4').feature('lngr9').set('unit', 'mol/m^3'); model.result('pg4').feature('lngr9').set('descr', 'Concentration'); model.result('pg4').feature('lngr9').set('legend', true); model.result('pg4').feature('lngr9').set('legendmethod', 'manual');

model.result('pg4').feature('lngr9').set('legends', {'CH3OH'}); model.result('pg4').feature('lngr9').set('smooth', 'none'); model.result('pg4').feature('lngr10').name('CH4'); model.result('pg4').feature('lngr10').set('data', 'cln1'); model.result('pg4').feature('lngr10').set('expr', 'cCH4'); model.result('pg4').feature('lngr10').set('unit', 'mol/m^3'); model.result('pg4').feature('lngr10').set('descr', 'Concentration'); model.result('pg4').feature('lngr10').set('legend', true); model.result('pg4').feature('lngr10').set('legendmethod', 'manual'); model.result('pg4').feature('lngr10').set('legends', {'CH4'}); model.result('pg4').feature('lngr10').set('smooth', 'none'); model.result('pg4').feature('lngr11').name('H2'); model.result('pg4').feature('lngr11').set('data', 'cln1'); model.result('pg4').feature('lngr11').set('expr', 'cH2'); model.result('pg4').feature('lngr11').set('unit', 'mol/m^3'); model.result('pg4').feature('lngr11').set('descr', 'Concentration'); model.result('pg4').feature('lngr11').set('legend', true); model.result('pg4').feature('lngr11').set('legendmethod', 'manual'); model.result('pg4').feature('lngr11').set('legends', {'H2'}); model.result('pg4').feature('lngr11').set('smooth', 'none'); model.result('pg4').feature('lngr12').set('data', 'cln1'); model.result('pg4').feature('lngr12').set('expr', 'C_balance'); model.result('pg4').feature('lngr12').set('unit', 'mol/m^3'); model.result('pg4').feature('lngr12').set('descr', ''); model.result('pg4').feature('lngr12').set('linestyle', 'dotted'); model.result('pg4').feature('lngr12').set('linecolor', 'black'); model.result('pg4').feature('lngr12').set('legend', true); model.result('pg4').feature('lngr12').set('legendmethod', 'manual'); model.result('pg4').feature('lngr12').set('legends', {'Total carbon'}); model.result('pg4').feature('lngr12').set('smooth', 'none'); model.result('pg5').name('velocity profile'); model.result('pg5').set('xlabel', 'Arc length'); model.result('pg5').set('ylabel', 'Velocity field, x component (m/s)'); model.result('pg5').set('xlabelactive', false); model.result('pg5').set('ylabelactive', false); model.result('pg5').feature('lngr1').set('data', 'cln2'); model.result('pg5').feature('lngr1').set('expr', 'u'); model.result('pg5').feature('lngr1').set('descr', 'Velocity field, x component'); model.result('pg5').feature('lngr1').set('smooth', 'none');

% Concentration of CO2

cCO2_1(1) = mphinterp(model, 'cCO2', 'coord', [1.12;0]);

cCO2_1(2) = mphinterp(model, 'cCO2', 'coord', [1.12;0.1]); cCO2_1(3) = mphinterp(model, 'cCO2', 'coord', [1.12;0.2]); cCO2_1(4) = mphinterp(model, 'cCO2', 'coord', [1.12;0.3]); cCO2_1(5) = mphinterp(model,'cCO2','coord',[1.12;0.4]); $cCO2_1(6) = mphinterp(model, cCO2', coord', [1.12; 0.5]);$ cCO2_2(1) = mphinterp(model, 'cCO2', 'coord', [2.24;0]); $cCO2_2(2) = mphinterp(model, cCO2', coord', [2.24; 0.1]);$ cCO2_2(3) = mphinterp(model, 'cCO2', 'coord', [2.24; 0.2]); cCO2_2(4) = mphinterp(model, 'cCO2', 'coord', [2.24;0.3]); cCO2_2(5) = mphinterp(model, 'cCO2', 'coord', [2.24;0.4]); cCO2_2(6) = mphinterp(model,'cCO2','coord',[2.24;0.5]); cCO2_3(1) = mphinterp(model, 'cCO2', 'coord', [5.6;0]); cCO2_3(2) = mphinterp(model, 'cCO2', 'coord', [5.6; 0.1]); $cCO2_3(3) = mphinterp(model, cCO2', coord', [5.6; 0.2]);$ cCO2_3(4) = mphinterp(model, 'cCO2', 'coord', [5.6; 0.3]); cCO2_3(5) = mphinterp(model, 'cCO2', 'coord', [5.6; 0.4]); cCO2_3(6) = mphinterp(model, 'cCO2', 'coord', [5.6; 0.5]); cCO2_4(1) = mphinterp(model,'cCO2','coord',[11.2;0]); $cCO2_4(2) = mphinterp(model, cCO2', coord', [11.2; 0.1]);$ cCO2_4(3) = mphinterp(model,'cCO2','coord',[11.2;0.2]); $cCO2_4(4) = mphinterp(model, cCO2', coord', [11.2; 0.3]);$ cCO2_4(5) = mphinterp(model, 'cCO2', 'coord', [11.2;0.4]); cCO2_4(6) = mphinterp(model, 'cCO2', 'coord', [11.2;0.5]); cCO2_5(1) = mphinterp(model, 'cCO2', 'coord', [22.4;0]); cCO2_5(2) = mphinterp(model,'cCO2','coord',[22.4;0.1]); cCO2_5(3) = mphinterp(model, 'cCO2', 'coord', [22.4;0.2]); cCO2_5(4) = mphinterp(model, 'cCO2', 'coord', [22.4;0.3]); $cCO2_5(5) = mphinterp(model, cCO2', coord', [22.4; 0.4]);$ cCO2_5(6) = mphinterp(model, 'cCO2', 'coord', [22.4;0.5]);

 $cCO2_mod_1 = mean([cCO2_1(1) cCO2_1(2) cCO2_1(3) cCO2_1(4) cCO2_1(5) cCO2_1(6)]);$ $cCO2_mod_2 = mean([cCO2_2(1) cCO2_2(2) cCO2_2(3) cCO2_2(4) cCO2_2(5) cCO2_2(6)]);$ $cCO2_mod_3 = mean([cCO2_3(1) cCO2_3(2) cCO2_3(3) cCO2_3(4) cCO2_3(5) cCO2_3(6)]);$ $cCO2_mod_4 = mean([cCO2_4(1) cCO2_4(2) cCO2_4(3) cCO2_4(4) cCO2_4(5) cCO2_4(6)]);$ $cCO2_mod_5 = mean([cCO2_5(1) cCO2_5(2) cCO2_5(3) cCO2_5(4) cCO2_5(5) cCO2_5(6)]);$

% Concentration of HCOOH

cHCOOH_1(1) = mphinterp(model,'cHCOOH','coord',[1.12;0]); cHCOOH_1(2) = mphinterp(model,'cHCOOH','coord',[1.12;0.1]); cHCOOH_1(3) = mphinterp(model,'cHCOOH','coord',[1.12;0.2]); cHCOOH_1(4) = mphinterp(model,'cHCOOH','coord',[1.12;0.3]); cHCOOH_1(5) = mphinterp(model,'cHCOOH','coord',[1.12;0.4]); cHCOOH_1(6) = mphinterp(model,'cHCOOH','coord',[1.12;0.5]); cHCOOH_2(1) = mphinterp(model,'cHCOOH','coord',[2.24;0]); cHCOOH_2(2) = mphinterp(model,'cHCOOH','coord',[2.24;0.1]); cHCOOH_2(3) = mphinterp(model,'cHCOOH','coord',[2.24;0.2]); cHCOOH_2(4) = mphinterp(model,'cHCOOH','coord',[2.24;0.3]); cHCOOH_2(5) = mphinterp(model,'cHCOOH','coord',[2.24;0.4]); cHCOOH_2(6) = mphinterp(model,'cHCOOH','coord',[2.24;0.5]); cHCOOH_3(1) = mphinterp(model,'cHCOOH','coord',[5.6;0]); cHCOOH_3(2) = mphinterp(model,'cHCOOH','coord',[5.6;0.1]); cHCOOH_3(3) = mphinterp(model,'cHCOOH','coord',[5.6;0.2]); cHCOOH_3(4) = mphinterp(model,'cHCOOH','coord',[5.6;0.3]); cHCOOH_3(5) = mphinterp(model,'cHCOOH','coord',[5.6;0.4]); cHCOOH_3(6) = mphinterp(model,'cHCOOH','coord',[5.6;0.5]); cHCOOH_4(1) = mphinterp(model,'cHCOOH','coord',[11.2;0]); cHCOOH_4(2) = mphinterp(model,'cHCOOH','coord',[11.2;0.1]); cHCOOH_4(3) = mphinterp(model,'cHCOOH','coord',[11.2;0.2]); cHCOOH_4(4) = mphinterp(model,'cHCOOH','coord',[11.2;0.3]); cHCOOH_4(5) = mphinterp(model,'cHCOOH','coord',[11.2;0.4]); cHCOOH_4(6) = mphinterp(model,'cHCOOH','coord',[11.2;0.5]); cHCOOH_5(1) = mphinterp(model,'cHCOOH','coord',[22.4;0]); cHCOOH_5(2) = mphinterp(model,'cHCOOH','coord',[22.4;0.1]); cHCOOH_5(3) = mphinterp(model,'cHCOOH','coord',[22.4;0.2]); cHCOOH_5(4) = mphinterp(model,'cHCOOH','coord',[22.4;0.3]); cHCOOH_5(5) = mphinterp(model,'cHCOOH','coord',[22.4;0.4]); cHCOOH_5(6) = mphinterp(model,'cHCOOH','coord',[22.4;0.5]);

cHCOOH_mod_1 = mean([cHCOOH_1(1) cHCOOH_1(2) cHCOOH_1(3) cHCOOH_1(4) cHCOOH_1(5) cHCOOH_1(6)]); cHCOOH_mod_2 = mean([cHCOOH_2(1) cHCOOH_2(2) cHCOOH_2(3) cHCOOH_2(4) cHCOOH_2(5) cHCOOH_2(6)]); cHCOOH_mod_3 = mean([cHCOOH_3(1) cHCOOH_3(2) cHCOOH_3(3) cHCOOH_3(4) cHCOOH_3(5) cHCOOH_3(6)]); cHCOOH_mod_4 = mean([cHCOOH_4(1) cHCOOH_4(2) cHCOOH_4(3) cHCOOH_4(4) cHCOOH_4(5) cHCOOH_4(6)]); cHCOOH_mod_5 = mean([cHCOOH_5(1) cHCOOH_5(2) cHCOOH_5(3) cHCOOH_5(4) cHCOOH_5(5) cHCOOH_5(6)]);

% Concentration of HCHO

cHCHO_1(1) = mphinterp(model,'cHCHO','coord',[1.12;0]); cHCHO_1(2) = mphinterp(model,'cHCHO','coord',[1.12;0.1]); cHCHO_1(3) = mphinterp(model,'cHCHO','coord',[1.12;0.2]); cHCHO_1(4) = mphinterp(model,'cHCHO','coord',[1.12;0.3]); cHCHO_1(5) = mphinterp(model,'cHCHO','coord',[1.12;0.4]); cHCHO_1(6) = mphinterp(model,'cHCHO','coord',[1.12;0.5]); cHCHO_2(1) = mphinterp(model, 'cHCHO', 'coord', [2.24;0]); cHCHO_2(2) = mphinterp(model,'cHCHO','coord',[2.24;0.1]); cHCHO_2(3) = mphinterp(model, 'cHCHO', 'coord', [2.24;0.2]); cHCHO_2(4) = mphinterp(model,'cHCHO','coord',[2.24;0.3]); cHCHO_2(5) = mphinterp(model, 'cHCHO', 'coord', [2.24;0.4]); cHCHO_2(6) = mphinterp(model,'cHCHO','coord',[2.24;0.5]); cHCHO_3(1) = mphinterp(model,'cHCHO','coord',[5.6;0]); cHCHO_3(2) = mphinterp(model, 'cHCHO', 'coord', [5.6;0.1]); cHCHO_3(3) = mphinterp(model,'cHCHO','coord',[5.6;0.2]); cHCHO_3(4) = mphinterp(model,'cHCHO','coord',[5.6;0.3]); cHCHO_3(5) = mphinterp(model,'cHCHO','coord',[5.6;0.4]); cHCHO_3(6) = mphinterp(model, 'cHCHO', 'coord', [5.6;0.5]); cHCHO_4(1) = mphinterp(model, 'cHCHO', 'coord', [11.2;0]); cHCHO_4(2) = mphinterp(model,'cHCHO','coord',[11.2;0.1]); cHCHO_4(3) = mphinterp(model,'cHCHO','coord',[11.2;0.2]); cHCHO_4(4) = mphinterp(model,'cHCHO','coord',[11.2;0.3]); cHCHO_4(5) = mphinterp(model, 'cHCHO', 'coord', [11.2;0.4]); cHCHO_4(6) = mphinterp(model,'cHCHO','coord',[11.2;0.5]); cHCHO_5(1) = mphinterp(model, 'cHCHO', 'coord', [22.4;0]); cHCHO_5(2) = mphinterp(model,'cHCHO','coord',[22.4;0.1]); cHCHO_5(3) = mphinterp(model,'cHCHO','coord',[22.4;0.2]); cHCHO_5(4) = mphinterp(model,'cHCHO','coord',[22.4;0.3]); cHCHO_5(5) = mphinterp(model,'cHCHO','coord',[22.4;0.4]); cHCHO_5(6) = mphinterp(model, 'cHCHO', 'coord', [22.4;0.5]);

cHCHO_mod_1 = mean([cHCHO_1(1) cHCHO_1(2) cHCHO_1(3) cHCHO_1(4) cHCHO_1(5) cHCHO_1(6)]); cHCHO_mod_2 = mean([cHCHO_2(1) cHCHO_2(2) cHCHO_2(3) cHCHO_2(4) cHCHO_2(5) cHCHO_2(6)]); cHCHO_mod_3 = mean([cHCHO_3(1) cHCHO_3(2) cHCHO_3(3) cHCHO_3(4) cHCHO_3(5) cHCHO_3(6)]); cHCHO_mod_4 = mean([cHCHO_4(1) cHCHO_4(2) cHCHO_4(3) cHCHO_4(4) cHCHO_4(5) cHCHO_4(6)]); cHCHO_mod_5 = mean([cHCHO_5(1) cHCHO_5(2) cHCHO_5(3) cHCHO_5(4) cHCHO_5(5) cHCHO_5(6)]);

% Concentration of CH3OH

cCH3OH_1(1) = mphinterp(model,'cCH3OH','coord',[1.12;0]); cCH3OH_1(2) = mphinterp(model,'cCH3OH','coord',[1.12;0.1]); cCH3OH_1(3) = mphinterp(model,'cCH3OH','coord',[1.12;0.2]); cCH3OH_1(4) = mphinterp(model,'cCH3OH','coord',[1.12;0.3]); cCH3OH_1(5) = mphinterp(model,'cCH3OH','coord',[1.12;0.4]); cCH3OH_1(6) = mphinterp(model,'cCH3OH','coord',[1.12;0.5]); cCH3OH_2(1) = mphinterp(model,'cCH3OH','coord',[2.24;0]); cCH3OH_2(2) = mphinterp(model,'cCH3OH','coord',[2.24;0.1]); cCH3OH_2(3) = mphinterp(model, 'cCH3OH', 'coord', [2.24;0.2]); cCH3OH_2(4) = mphinterp(model, 'cCH3OH', 'coord', [2.24;0.3]); cCH3OH_2(5) = mphinterp(model, 'cCH3OH', 'coord', [2.24;0.4]); cCH3OH_2(6) = mphinterp(model,'cCH3OH','coord',[2.24;0.5]); cCH3OH_3(1) = mphinterp(model, 'cCH3OH', 'coord', [5.6;0]); cCH3OH_3(2) = mphinterp(model,'cCH3OH','coord',[5.6;0.1]); cCH3OH_3(3) = mphinterp(model, cCH3OH', coord', [5.6;0.2]); cCH3OH_3(4) = mphinterp(model,'cCH3OH','coord',[5.6;0.3]); cCH3OH_3(5) = mphinterp(model,'cCH3OH','coord',[5.6;0.4]); cCH3OH_3(6) = mphinterp(model, cCH3OH', coord', [5.6;0.5]); cCH3OH_4(1) = mphinterp(model,'cCH3OH','coord',[11.2;0]); cCH3OH_4(2) = mphinterp(model, 'cCH3OH', 'coord', [11.2;0.1]); cCH3OH_4(3) = mphinterp(model, 'cCH3OH', 'coord', [11.2;0.2]); $cCH3OH_4(4) = mphinterp(model, cCH3OH', coord', [11.2; 0.3]);$ cCH3OH_4(5) = mphinterp(model, cCH3OH', coord', [11.2;0.4]); cCH3OH_4(6) = mphinterp(model, 'cCH3OH', 'coord', [11.2;0.5]); cCH3OH_5(1) = mphinterp(model,'cCH3OH','coord',[22.4;0]); cCH3OH_5(2) = mphinterp(model,'cCH3OH','coord',[22.4;0.1]); cCH3OH_5(3) = mphinterp(model, 'cCH3OH', 'coord', [22.4;0.2]); cCH3OH_5(4) = mphinterp(model, 'cCH3OH', 'coord', [22.4;0.3]); cCH3OH_5(5) = mphinterp(model, 'cCH3OH', 'coord', [22.4;0.4]); cCH3OH_5(6) = mphinterp(model, 'cCH3OH', 'coord', [22.4;0.5]);

cCH3OH_mod_1 = mean([cCH3OH_1(1) cCH3OH_1(2) cCH3OH_1(3) cCH3OH_1(4) cCH3OH_1(5) cCH3OH_1(6)]);

cCH3OH_mod_2 = mean([cCH3OH_2(1) cCH3OH_2(2) cCH3OH_2(3) cCH3OH_2(4) cCH3OH_2(5) cCH3OH_2(6)]);

cCH3OH_mod_3 = mean([cCH3OH_3(1) cCH3OH_3(2) cCH3OH_3(3) cCH3OH_3(4) cCH3OH_3(5) cCH3OH_3(6)]);

cCH3OH_mod_4 = mean([cCH3OH_4(1) cCH3OH_4(2) cCH3OH_4(3) cCH3OH_4(4) cCH3OH_4(5) cCH3OH_4(6)]);

cCH3OH_mod_5 = mean([cCH3OH_5(1) cCH3OH_5(2) cCH3OH_5(3) cCH3OH_5(4) cCH3OH_5(5) cCH3OH_5(6)]);

% Concentration of CH4

cCH4_1(1) = mphinterp(model,'cCH4','coord',[1.12;0]); cCH4_1(2) = mphinterp(model,'cCH4','coord',[1.12;0.1]); cCH4_1(3) = mphinterp(model,'cCH4','coord',[1.12;0.2]); cCH4_1(4) = mphinterp(model,'cCH4','coord',[1.12;0.3]); cCH4_1(5) = mphinterp(model,'cCH4','coord',[1.12;0.4]); cCH4_1(6) = mphinterp(model,'cCH4','coord',[1.12;0.5]); cCH4_2(1) = mphinterp(model,'cCH4','coord',[2.24;0]); cCH4_2(2) = mphinterp(model, 'cCH4', 'coord', [2.24;0.1]); cCH4_2(3) = mphinterp(model, 'cCH4', 'coord', [2.24; 0.2]); cCH4_2(4) = mphinterp(model, 'cCH4', 'coord', [2.24;0.3]); cCH4_2(5) = mphinterp(model,'cCH4','coord',[2.24;0.4]); cCH4_2(6) = mphinterp(model, 'cCH4', 'coord', [2.24;0.5]); cCH4_3(1) = mphinterp(model,'cCH4','coord',[5.6;0]); $cCH4_3(2) = mphinterp(model, cCH4', coord', [5.6; 0.1]);$ cCH4_3(3) = mphinterp(model, 'cCH4', 'coord', [5.6; 0.2]); cCH4_3(4) = mphinterp(model, 'cCH4', 'coord', [5.6;0.3]); cCH4_3(5) = mphinterp(model, 'cCH4', 'coord', [5.6;0.4]); cCH4_3(6) = mphinterp(model,'cCH4','coord',[5.6;0.5]); cCH4_4(1) = mphinterp(model, 'cCH4', 'coord', [11.2;0]); cCH4_4(2) = mphinterp(model, 'cCH4', 'coord', [11.2;0.1]); cCH4_4(3) = mphinterp(model, 'cCH4', 'coord', [11.2;0.2]); cCH4_4(4) = mphinterp(model,'cCH4','coord',[11.2;0.3]); cCH4_4(5) = mphinterp(model,'cCH4','coord',[11.2;0.4]); cCH4_4(6) = mphinterp(model, 'cCH4', 'coord', [11.2;0.5]); cCH4_5(1) = mphinterp(model,'cCH4','coord',[22.4;0]); cCH4_5(2) = mphinterp(model,'cCH4','coord',[22.4;0.1]); cCH4_5(3) = mphinterp(model,'cCH4','coord',[22.4;0.2]); cCH4_5(4) = mphinterp(model, 'cCH4', 'coord', [22.4;0.3]); cCH4_5(5) = mphinterp(model, 'cCH4', 'coord', [22.4;0.4]); cCH4_5(6) = mphinterp(model, 'cCH4', 'coord', [22.4;0.5]);

 $cCH4_mod_1 = mean([cCH4_1(1) cCH4_1(2) cCH4_1(3) cCH4_1(4) cCH4_1(5) cCH4_1(6)]);$ $cCH4_mod_2 = mean([cCH4_2(1) cCH4_2(2) cCH4_2(3) cCH4_2(4) cCH4_2(5) cCH4_2(6)]);$ $cCH4_mod_3 = mean([cCH4_3(1) cCH4_3(2) cCH4_3(3) cCH4_3(4) cCH4_3(5) cCH4_3(6)]);$ $cCH4_mod_4 = mean([cCH4_4(1) cCH4_4(2) cCH4_4(3) cCH4_4(4) cCH4_4(5) cCH4_4(6)]);$ $cCH4_mod_5 = mean([cCH4_5(1) cCH4_5(2) cCH4_5(3) cCH4_5(4) cCH4_5(5) cCH4_5(6)]);$

% Concentration of H2

 $cH2_1(1) = mphinterp(model,'cH2','coord',[1.12;0]);\\ cH2_1(2) = mphinterp(model,'cH2','coord',[1.12;0.1]);\\ cH2_1(3) = mphinterp(model,'cH2','coord',[1.12;0.2]);\\ cH2_1(4) = mphinterp(model,'cH2','coord',[1.12;0.3]);\\ cH2_1(5) = mphinterp(model,'cH2','coord',[1.12;0.4]);\\ cH2_1(6) = mphinterp(model,'cH2','coord',[1.12;0.5]);\\ cH2_2(1) = mphinterp(model,'cH2','coord',[2.24;0]);\\ cH2_2(2) = mphinterp(model,'cH2','coord',[2.24;0.1]);\\ cH2_2(3) = mphinterp(model,'cH2','coord',[2.24;0.2]);\\ cH2_2(4) = mphinterp(model,'cH2','coord',[2.24;0.3]);\\ cH2_2(5) = mphinterp(model,'cH2','coord',[2.24;0.4]);\\ cH2_2(5) = mp$

cH2_2(6) = mphinterp(model, 'cH2', 'coord', [2.24;0.5]); cH2_3(1) = mphinterp(model,'cH2','coord',[5.6;0]); cH2_3(2) = mphinterp(model,'cH2','coord',[5.6;0.1]); cH2_3(3) = mphinterp(model,'cH2','coord',[5.6;0.2]); cH2_3(4) = mphinterp(model,'cH2','coord',[5.6;0.3]); cH2_3(5) = mphinterp(model,'cH2','coord',[5.6;0.4]); cH2_3(6) = mphinterp(model,'cH2','coord',[5.6;0.5]); cH2_4(1) = mphinterp(model,'cH2','coord',[11.2;0]); cH2_4(2) = mphinterp(model,'cH2','coord',[11.2;0.1]); cH2_4(3) = mphinterp(model, 'cH2', 'coord', [11.2;0.2]); cH2_4(4) = mphinterp(model,'cH2','coord',[11.2;0.3]); cH2_4(5) = mphinterp(model,'cH2','coord',[11.2;0.4]); cH2_4(6) = mphinterp(model,'cH2','coord',[11.2;0.5]); cH2_5(1) = mphinterp(model,'cH2','coord',[22.4;0]); cH2_5(2) = mphinterp(model,'cH2','coord',[22.4;0.1]); cH2_5(3) = mphinterp(model,'cH2','coord',[22.4;0.2]); cH2_5(4) = mphinterp(model,'cH2','coord',[22.4;0.3]); cH2_5(5) = mphinterp(model,'cH2','coord',[22.4;0.4]); cH2_5(6) = mphinterp(model,'cH2','coord',[22.4;0.5]);

```
cH2\_mod\_1 = mean([cH2\_1(1) cH2\_1(2) cH2\_1(3) cH2\_1(4) cH2\_1(5) cH2\_1(6)]);\\ cH2\_mod\_2 = mean([cH2\_2(1) cH2\_2(2) cH2\_2(3) cH2\_2(4) cH2\_2(5) cH2\_2(6)]);\\ cH2\_mod\_3 = mean([cH2\_3(1) cH2\_3(2) cH2\_3(3) cH2\_3(4) cH2\_3(5) cH2\_3(6)]);\\ cH2\_mod\_4 = mean([cH2\_4(1) cH2\_4(2) cH2\_4(3) cH2\_4(4) cH2\_4(5) cH2\_4(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(1) cH2\_5(2) cH2\_5(3) cH2\_5(4) cH2\_5(5) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(1) cH2\_5(2) cH2\_5(3) cH2\_5(5) cH2\_5(5) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(1) cH2\_5(2) cH2\_5(3) cH2\_5(4) cH2\_5(5) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(1) cH2\_5(2) cH2\_5(3) cH2\_5(5) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(1) cH2\_5(2) cH2\_5(3) cH2\_5(5) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(1) cH2\_5(2) cH2\_5(5) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(1) cH2\_5(2) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(1) cH2\_5(2) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(1) cH2\_5(2) cH2\_5(2) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(2) cH2\_5(2) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(2) cH2\_5(2) cH2\_5(2) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(2) cH2\_5(2) cH2\_5(2) cH2\_5(6)]);\\ cH2\_mod\_5 = mean([cH2\_5(2) cH2\_5(2) cH2\_5
```

```
cCO2_exp = [18.836 11.309 4.686 3.698 1.768];
cHCOOH_exp = [0.004 0.003 0.002 0.001 0.001];
cHCHO_exp = [10.083 13.910 15.774 9.885 5.283];
cCH3OH_exp = [3.124 5.026 9.058 11.968 8.924];
cCH4_exp = [1.627 2.782 4.393 9.193 19.999];
cH2_exp = [12.872 20.538 30.089 36.988 49.945];
```

 $f_CO2 =$

(cCO2_mod_1-cCO2_exp(1))^2+(cCO2_mod_2-cCO2_exp(2))^2+(cCO2_mod_3-cCO2_exp(3))^2+(cCO2_mod_4-cCO2_exp(4))^2+(cCO2_mod_5-cCO2_exp(5))^2;

 $f_HCOOH =$

 $(cHCOOH_mod_1-cHCOOH_exp(1))^{2}+(cHCOOH_mod_2-cHCOOH_exp(2))^{2}+(cHCOOH_mod_3-cHCOOH_exp(3))^{2}+(cHCOOH_mod_4-cHCOOH_exp(4))^{2}+(cHCOOH_mod_5-cHCOOH_exp(5))^{2};$

 $f_HCHO =$

 $(cHCHO_mod_1-cHCHO_exp(1))^{2}+(cHCHO_mod_2-cHCHO_exp(2))^{2}+(cHCHO_mod_3-cHCHO_exp(3))^{2}+(cHCHO_mod_4-cHCHO_exp(4))^{2}+(cHCHO_mod_5-cHCHO_exp(5))^{2};$

 $f_CH3OH =$

(cCH3OH_mod_1-cCH3OH_exp(1))^2+(cCH3OH_mod_2-cCH3OH_exp(2))^2+(cCH3OH_mod_3-cCH3OH_exp(3))^2+(cCH3OH_mod_4-cCH3OH_exp(4))^2+(cCH3OH_mod_5-cCH3OH_exp(5))^2; f_CH4 =

 $(cCH4_mod_1-cCH4_exp(1))^{2}+(cCH4_mod_2-cCH4_exp(2))^{2}+(cCH4_mod_3-cCH4_exp(3))^{2}+(cCH4_mod_4-cCH4_exp(4))^{2}+(cCH4_mod_5-cCH4_exp(5))^{2};$

```
f_H2 =
```

 $(cH2_mod_1-cH2_exp(1))^{2}+(cH2_mod_2-cH2_exp(2))^{2}+(cH2_mod_3-cH2_exp(3))^{2}+(cH2_mod_4-cH2_exp(4))^{2}+(cH2_mod_5-cH2_exp(5))^{2};$

 $f = f_CO2+f_HCOOH+f_HCHO+f_CH3OH+f_CH4+f_H2;$

Results:

For reaction in aqueous solution,

Optimization terminated:

the current x satisfies the termination criteria using OPTIONS.TolX of 1.000000e-04 and F(X) satisfies the convergence criteria using OPTIONS.TolFun of 1.000000e-01

```
>> k
```

```
k =
0.0302 0.0027 0.9810 9.8165e-04 0.0048 0.0033
>> fval
fval =
738.6776
>> exitflag
exitflag =
1
```

For reaction in ionic liquid solution,

Optimization terminated:

the current x satisfies the termination criteria using OPTIONS.TolX of 1.000000e-04 and F(X) satisfies the convergence criteria using OPTIONS.TolFun of 1.000000e-01

```
>> k
```

k = 1.6524e-05 0.0064 1.4821 8.4004e-04 0.0019 0.0219 >> fval fval = 24665.2 >> exitflag exitflag = 1
Appendix D. Calibration Data Analysis

1. Relative uncertainty

The procedure of calculating the relative uncertainty is shown below:

(1) Calculate the average

$$\overline{A} = \frac{A_1 + A_2 + \dots + A_N}{N}$$

(2) Calculate the standard deviation

$$\sigma = \sqrt{\frac{\sum_{i=N}^{1} \left(A_i - \overline{A}\right)^2}{N - 1}}$$

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

$$\sigma_m = \frac{\sigma}{\sqrt{N}}$$

(4) Determine the relative uncertainty

Relative uncertainty =
$$\frac{\sigma_m}{\overline{A}}$$

The results are shown in the table below:

Volume of added acid (mL) Concentration Standard Relative Average Deviation (ppm) Uncertainty 3 1 2 300 8.468 8.610 8.598 8.325 0.066 0.65% 240 7.472 6.710 7.028 7.070 0.383 3.83% 180 5.218 5.678 5.108 5.335 0.302 4.01% 120 3.605 0.234 4.83% 3.156 3.492 3.418 60 1.736 2.371 1.876 2.088 0.160 11.83%

Table D-1. Relative Uncertainty of Volumes of Added Acid in NaHCO₃ Solutions

Matarial	Concentration	Peak	x Area (mV	·sec)	Avorago	Standard	Relative
1,14001141	(ppm)	1	2	3	Average	Deviation	Uncertainty
	10000	92.5204	79.7756	75.1516	82.4825	8.9952	6.30%
СН₃ОН	1000	10.5784	8.3438	8.5978	9.1733	1.2234	7.70%
	100	1.3792	1.6278	1.7309	1.5793	0.1808	6.61%
	10	0.8808	0.8644	0.9760	0.9071	0.0603	3.84%
	1900	6.9276	6.9274	6.8041	6.8864	0.0712	0.60%
нсно	380	1.9100	1.7469	1.9442	1.8670	0.1054	3.26%
	190	1.1390	1.3308	1.1852	1.2183	0.1001	4.74%
	38	0.7006	0.6952	0.7340	0.7099	0.0210	1.71%

Table D-2. Relative Uncertainty of Peak Areas of CH₃OH and HCHO

 Table D-3. Relative Uncertainty of Peak Areas of CH4

Concentration		Peak	Area (mV·s	ec)		Average	Standard	Relative
(ppm)	1	2	3	4	5	Average	Deviation	Uncertainty
1000	125.3088	101.3082	132.5274	90.1118	90.3820	107.928	19.851	13.01%
500	36.2720	46.3128	51.3130	52.1908	39.0748	45.033	7.151	11.23%
100	11.8104	13.8868	15.3576	13.2836	14.7406	13.816	1.373	7.03%
50	4.8972	3.7568	5.8584	6.2618	6.2592	5.407	1.077	14.09%
10	1.1228	0.9040	1.2688	1.0148	0.9867	1.059	0.141	9.40%

Concentration	Pea	k Area (mV∙	sec)	Average	Standard	Relative	
(ppm)	1	2	3	menage	Deviation	Uncertainty	
200	67824.5	77728	80743.5	75432	6758.6	6.34%	
100	37820.5	39398.5	40519	39246	1355.7	2.44%	
50	24562	25042	25296.5	24966.8	373.0	1.06%	
10	9527.5	8584.5	8120	8744	717.2	5.80%	

Concentration	Pe	ak Area (µS∙m	in)	Average	Standard	Relative
(ppm)	1	2	3		Deviation	Uncertainty
1	0.0753	0.0742	0.0755	0.0750	0.001	0.66%
5	0.3551	0.3895	0.3856	0.3767	0.019	3.54%
10	0.7579	0.7398	0.7356	0.7444	0.012	1.13%
50	4.1352	4.2803	4.3219	4.2458	0.098	1.63%
100	8.3108	8.3073	8.2665	8.2949	0.025	0.21%

 Table D-5. Relative Uncertainty of Peak Areas of HCOOH

Table D-6. Relative Uncertainty of Conductivities of KCOOH, KOH and K₂CO₃

Motorial	Concentration	Condu	ıctivity (µ	ıS/cm)	Avonogo	Standard	Relative
Wateria	(ppm)	1	2	3	Average	Deviation	Uncertainty
	1000	1270	1280	1290	1280.0	10.0	0.45%
	500	638	639	641	639.3	1.5	0.14%
КСООН	100	128	126	127	127.0	1.0	0.45%
	50	74.8	75.3	72.3	74.1	1.6	1.25%
	10	16.1	15	14.9	15.3	0.7	2.51%
	1000	5410	5420	5400	5410.0	10.0	0.11%
	500	2640	2750	2760	2716.7	66.6	1.42%
КОН	100	450	446	451	449.0	2.6	0.34%
	50	214	203	198	205.0	8.2	2.31%
	10	29.8	32.4	30.6	30.9	1.3	2.49%
	1000	2350	2300	2250	2300.0	50.0	1.26%
	500	1110	1150	1120	1126.7	20.8	1.07%
K ₂ CO ₃	100	224	225	226	225.0	1.0	0.26%
	50	93.3	93.5	93.2	93.3	0.2	0.09%
	10	24.7	24.1	25.3	24.7	0.6	1.40%

Concentration Absorbance Standard Relative Average (mol/m^3) Deviation Uncertainty 1 2 3 0.0060 506.48 0.0067 0.0060 0.0053 6.85E-04 8.06% 675.30 0.0093 0.0098 0.0100 0.0097 3.62E-04 2.64% 992.42 0.0155 0.0156 0.0157 0.0156 1.01E-04 0.46%

 Table D-7. Relative Uncertainty of Absorbance of CO2 in Ionic Liquid

2. Dixon's test

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

(1) Calculate the range

 $w = A_{\rm max} - A_{\rm min}$

(2) Calculate the gap

$$d = |A_{\text{questionable}} - A_{\text{neighbour}}|$$

(3) Calculate the Q value

$$Q = \frac{d}{w}$$

(4) Look up the Q value in the Dixon test Table according to the measurement number. We choose confidence interval as 95%. If Q>Q_{table} (In this case, $Q_{table} = 0.941$), the datum is an outlier, so we need to reject it; if Q<Q_{table}, the datum is not an outlier. The result of the Dixon's test is shown in the table below.

Test		Level of significance α							
Statistic	N	0.30	0.20	0.10	0.05	0.02	0.01	0.005	
	3	0.684	0.781	0.886	0.941	0.976	0.988	0.994	
Xo - Xi	4	0.471	0.560	0.679	0.765	0.846	0.889	0.926	
$r_{10} = \frac{x_2 - x_1}{x_p - x_1}$	5	0.373	0.451	0.557	0.642	0.729	0.780	0.821	
11 1	6	0.318	0.386	0.482	0.560	0.644	0.698	0.740	
	7	0.281	0.344	0.434	0.507	0.596	0.637	0.680	

Table D-8. Critical Values for the Dixon's Test of Outliers

						1		
Material	Concentration	A _{max}	A _{min}	W	$\mathbf{A}_{ ext{questionable}}$	d	Q	Outlier or not
	300	8.610	8.468	0.142	8.468	0.130	0.915	No
	240	7.472	6.710	0.762	7.472	0.444	0.583	No
NaHCO ₃	180	5.678	5.108	0.570	5.678	0.460	0.807	No
	120	3.605	3.156	0.449	3.156	0.336	0.748	No
	60	2.371	1.736	0.635	2.371	0.495	0.780	No
	10000	92.5204	75.1516	17.3688	92.5204	12.7448	0.734	No
CUL OU	1000	10.5784	8.3438	2.2346	10.5784	1.9806	0.886	No
CH ₃ OH	100	1.7309	1.3792	0.3517	1.3792	0.2486	0.707	No
	10	0.9760	0.8644	0.1116	0.9760	0.0952	0.853	No
	1900	6.9276	6.8041	0.1235	6.8041	0.1233	0.998	One
UCUO	380	1.9442	1.7469	0.1973	1.7469	0.1631	0.827	No
нсно	190	1.3308	1.1390	0.1918	1.3308	0.1456	0.759	No
	38	0.7340	0.6952	0.0388	0.7340	0.0334	0.861	No
	1000	132.5274	90.1118	42.4156	132.5274	7.2186	0.170	No
	500	52.1908	36.2720	15.9188	36.2720	2.8028	0.176	No
CH_4	100	15.3576	11.8104	3.5472	11.8104	1.4732	0.415	No
	50	6.2618	3.7568	2.5050	3.7568	1.1404	0.455	No
	10	1.2688	0.9040	0.3648	1.2688	0.1460	0.400	No
	1	0.0755	0.0742	0.0013	0.0742	0.0011	0.846	No
	5	0.3895	0.3551	0.0344	0.3551	0.0305	0.887	No
НСООН	10	0.7579	0.7356	0.0223	0.7579	0.0181	0.812	No
	50	4.3219	4.1352	0.1867	4.1352	0.1451	0.777	No
	100	8.3108	8.2665	0.0443	8.2665	0.0408	0.921	No

 Table D-9. Results of the Dixon's Test for Measured Species

(Table D-9 Continued)

	200	80743.5	67824.5	12919	67824.5	9903.5	0.767	No
TT	100	40519	37820.5	2698.5	37820.5	1578	0.585	No
Π_2	50	25296.5	24562	734.5	24562	480	0.654	No
	10	9527.5	8120	1407.5	8120	464.5	0.330	No
	1000	1290	1270	20	1270	10	0.500	No
	500	641	638	3	641	2	0.667	No
КСООН	100	128	126	2	128	1	0.500	No
	50	75.3	72.3	3	72.3	2.5	0.833	No
	10	16.1	14.9	1.2	16.1	1.1	0.917	No
	1000	5420	5400	20	5420	10	0.500	No
КОН	500	2760	2640	120	2640	110	0.917	No
	100	451	446	5	446	4	0.800	No
	50	214	198	16	214	11	0.688	No
	10	32.4	29.8	2.6	32.4	1.8	0.692	No
	1000	2350	2250	100	2350	50	0.500	No
	500	1150	1110	40	1150	30	0.750	No
K ₂ CO ₃	100	226	224	2	224	1	0.500	No
	50	93.5	93.2	0.3	93.5	0.2	0.667	No
	10	25.3	24.1	1.2	24.1	0.6	0.500	No
	506.48mol/m ³	0.0067	0.0053	0.0014	0.0053	0.0007	0.536	No
CO_2	675.30mol/m ³	0.0100	0.0093	0.0007	0.0093	0.0005	0.650	No
	992.42mol/m ³	0.0157	0.0155	0.0002	0.0155	0.0001	0.598	No

3. Calibration Curve with Error Bars

The procedure of determining the error bars is shown as below:

(1) Calculate the average

$$\overline{A} = \frac{A_1 + A_2 + \dots + A_N}{N}$$

(2) Calculate the standard error

$$\sigma_m = \sqrt{\frac{\sum_{i=N}^{1} \left(A_i - \overline{A}\right)^2}{N(N-1)}}$$

(3) The error bars are drawn at σ_m level ($\overline{A} \pm \sigma_m$)

The results are shown in the table below:

Table D-10. Standard Error of Volumes of Added Acid in Narie 03									
Concentration (ppm)	300	240	180	120	60				
Standard Error	0.134	0.271	0.214	0.165	0.236				

Table D-10. Standard Error of Volumes of Added Acid in NaHCO₃

Table D-11. Standard Error of Feak Areas of CH3011									
Concentration	10000	1000	100	10					
(ppm)	20000	2000	200						
Standard Error	5.193	0.706	0.104	0.035					

Table D-11. Standard Error of Peak Areas of CH₃OH

Table D-12. Standard Error of Peak Areas of HCHO

Concentration (ppm)	1900	380	190	38
Standard Error	0.041	0.133	0.064	0.012

Table D-13. Standard Error of Peak Areas of CH₄

Concentration (ppm)	1000	500	100	50	10
Standard Error	14.037	5.057	0.971	0.762	0.100

Table D-14. Standard Error of Peak Areas of H₂

Concentration (ppm)	200	100	50	10
Standard Error	4779.061	958.623	263.733	507.121

Table D-15. Standard Error of Peak Areas of HCOOH

Concentration (ppm)	100	50	10	5	1
Standard Error	0.0174	0.0693	0.0084	0.0133	0.0005

Concentration (ppm)	1000	500	100	50	10
Standard Error of KCOOH	5.774	0.882	0.577	0.928	0.384
Standard Error of KOH	5.774	38.442	1.528	4.726	0.769
Standard Error of K ₂ CO ₃	28.868	12.019	0.577	0.088	0.346

Table D-16. Standard Error of Conductivities of KCOOH, KOH and K₂CO₃

Table D-17. Standard Error of Absorbance of CO₂ in Ionic Liquid

Concentration (mol/m ³)	506.48	675.30	992.42	
Standard Error	4.84E-04	2.56E-04	7.11E-05	

- 4. Determination of the Best Fit Line
- (1) Recalculate the best fit line

For fit line y=mx+b,

$$m = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{N \sum x_i^2 - \left(\sum x_i\right)^2} \qquad b = \overline{y} - \overline{m}$$

If this fit line is forced to pass through origin or a point on y-axis,

$$m = \frac{\sum x_i y_i - b \sum x_i}{\sum x_i^2}$$

Material	$\sum x_i$	$\frac{1}{x}$	$\sum y_i$	\overline{y}	$\sum x_i y_i$	$\sum x_i^2$	т	b
NaHCO ₃	2700	180	78.126	5.275	17263.26	594000	0.0291	0
CH ₃ OH	33330	2777.5	282.427	23.536	2502497	303030300	0.0082	0.8615
НСНО	7524	627	32.045	2.670	42156.09	11375832	0.0033	0.5927
CH_4	8300	332	866.211	34.648	660532.4	6313000	0.1046	0
H_2	1080	90	445166.5	37097.21	61040345	157800	333.42	7802.5
НСООН	498	33.2	41.211	2.747	3153.539	37878	0.0833	0
КСООН	4980	332	6407.4	427.16	4848680	3787800	1.2792	0.64
KOH	4980	332	26434.8	1762.32	20471378	3787800	5.4037	0.64
K ₂ CO ₃	4980	332	11309.1	753.94	8672241	3787800	2.2887	0.64
CO_2	6522.6	724.7	0.094	0.010	75.240	5092366	2.0E-5	-0.0038

 Table D-18. Result of Recalculating the Best-fit Line

(2) Calculate the uncertainties of slope and intercept

Uncertainty in y:
$$s_y = \sqrt{\frac{\sum_{i=1}^{n} (y_i - mx)^2}{N - 2}}$$

Uncertainty in the slope:
$$s_m = \sqrt{\frac{s_y^2}{\sum (\bar{x} - x_i)^2}}$$

Uncertainty in the intercept:
$$s_b = s_y \sqrt{\frac{1}{N - (\sum x_i)^2 / \sum x_i^2}}$$

(3) Calculate the uncertainty in the concentration:

Uncertainty in the regression:
$$s_r = \sqrt{\frac{\left|\sum \left(y_i - \overline{y}\right)^2 - m^2 \sum \left(x_i - \overline{x}\right)^2\right|}{N - 2}}$$

Uncertainty in the concentration: $s_c = \frac{s_r}{m} \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{\left(\overline{y}_c - \overline{y}\right)^2}{m^2 \sum \left(x_i - \overline{x}\right)^2}}$

Table D-19. Result of Calculating the Uncertainties of Slope, Intercept andRegression

	Uncertainty in	Uncertainty in	Uncertainty in	Uncertainty in
Material	у	slope	intercept	regression
	s _y	S _m	s _b	S _r
NaHCO ₃	0.28772	0.00088	_	0.66448
CH ₃ OH	4.06195	0.00028	1.40704	4.06195
НСНО	0.07368	0.00003	0.02780	0.07368
CH_4	9.71115	0.00515	_	10.05039
H ₂	3574.07945	14.51871	_	7969.80088
НСООН	0.07227	0.00049	—	0.33445
КСООН	6.23919	0.00134	—	1566.06773
КОН	62.02038	0.04245	—	369.57261
K ₂ CO ₃	25.87071	0.01771	_	109.95222
CO ₂	0.00046	7.5526E-07	0.00057	0.00046

Concentration (ppm)	300	240	180	120	60
Uncertainty in Concentration	16.5	15.1	14.5	15.1	16.5

Table D-20. Uncertainty in Concentration for NaHCO₃

Table D-21. Uncertainty in Concentration for CH₃OH

Concentration (ppm)	10000	1000	100	10
Uncertainty in Concentration	405.6	326.8	334.2	335.0

Table D-22. Uncertainty in Concentration for HCHO

Concentration (ppm)	1900	380	190	38
Uncertainty in Concentration	18.1	14.5	14.8	15.2

Table D-23. Uncertainty in Concentration for CH₄

Concentration (ppm)	1000	500	100	50	10
Uncertainty in Concentration	59.0	47.3	48.1	49.2	49.8

Table D-24. Uncertainty in Concentration for H₂

Concentration (ppm)	200	100	50	10
Uncertainty in Concentration	19.0	15.4	15.8	17.5

Table D-25. Uncertainty in Concentration for HCOOH

Concentration (ppm)	100	50	10	5	1
Uncertainty in Concentration	3.1	2.6	2.6	2.7	2.7

Table D-26. Uncertainty in Concentration for KCOOH, KOH and K₂CO₃

Concentration (ppm)	1000	500	100	50	10
Uncertainty in Concentration of KCOOH	793.9	775.5	776.7	777.7	778.9
Uncertainty in Concentration of KOH	53.6	44.0	44.7	45.3	45.8
Uncertainty in Concentration of K ₂ CO ₃	37.6	30.9	31.3	31.8	32.1

Table D-27. Uncertainty in Concentration for CO₂ in Ionic Liquid

Concentration (mol/m ³)	506.48	675.30	992.42
Uncertainty in Concentration	17.8	15.6	18.5

5. Signal and Noise Test

The signal-to-noise ratio, S/N, is calculated by using the following equation:

$$S / N = \frac{A}{\sigma} = \frac{\text{mean}}{\text{standard deviation}}$$

Concentration (ppm)	300	240	180	120	60
Signal and Noise	108.7	18.5	17.6	14.6	6.0

Table D-29.	Result	of Signal	and Noise	Test for	CH ₃ OH
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Concentration (ppm)	10000	1000	100	10
Signal and Noise	9.2	7.5	8.7	15.1

Concentration (ppm)	1900	380	190	38
Signal and Noise	96.7	17.7	12.2	33.8

Table D-30. Result of Signal and Noise Test for HCHO

Table D-31. Result of Signal and Noise Test for CH₄

Concentration (ppm)	1000	500	100	50	10
Signal and Noise	5.4	6.3	10.1	5.0	7.5

Table D-32. Result of Signal and Noise Test for H₂

Concentration (ppm)	500	100	50	10
Signal and Noise	11.2	28.9	66.9	12.2

Table D-33. Result of Signal and Noise Test for HCOOH

Concentration (ppm)	100	50	10	5	1
Signal and Noise	336.8	43.3	62.8	20.0	107.1

Table D-34. Result of Signal and Noise Test for KCOOH, KOH and K₂CO₃

Concentration (ppm)	1000	500	100	50	10
Signal and Noise of KCOOH	128.0	418.5	127.0	46.1	23.0
Signal and Noise of KOH	541.0	40.8	169.7	25.0	23.2
Signal and Noise of K ₂ CO ₃	46.0	54.1	225.0	611.0	41.2

Concentration (mol/m ³)	506.48	675.30	992.42	
Signal and Noise	8.8	26.8	155.3	

Table D-35. Result of Signal and Noise Test for CO₂ in Ionic Liquid

Mean Residence Time (sec)	CO ₂ (mol/m ³)	HCOOH (mol/m ³)	HCHO (mol/m ³)	CH ₃ OH (mol/m ³)	CH ₄ (mol/m ³)	H ₂ (mol/m ³)
0	34.002	0.000	0.000	0.000	0.000	0.000
5	21.245	0.004	8.646	2.279	1.270	11.893
10	15.101	0.003	11.969	4.282	1.880	19.161
25	9.081	0.002	13.853	6.826	3.503	26.725
50	7.541	0.002	8.899	10.199	8.438	32.973
100	6.150	0.001	3.275	8.102	18.562	45.574

Table E-1. Experimental Data (20V Voltage, 500µm Spacer, Aqueous Solution)

Table E-2. Experimental Data (22.5V Voltage, 500µm Spacer, Aqueous Solution)

Mean Residence Time (sec)	CO ₂ (mol/m ³)	HCOOH (mol/m ³)	HCHO (mol/m ³)	CH ₃ OH (mol/m ³)	CH ₄ (mol/m ³)	H ₂ (mol/m ³)
0	34.002	0.000	0.000	0.000	0.000	0.000
5	18.836	0.004	10.083	3.124	1.627	12.872
10	11.309	0.003	13.910	5.026	2.782	20.538
25	4.686	0.002	15.774	9.058	4.393	30.089
50	3.698	0.001	9.885	11.968	9.193	36.988
100	1.768	0.001	5.283	8.924	19.999	49.945

Tuble L of Lapermiental Data (20, 1010 get 200 min Spacer, 11 quebus Solution)	Table E-3. Experimental Data (20V	VVoltage, 200µm Sp	acer, Aqueous Solution)
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Mean Residence Time (sec)	CO ₂ (mol/m ³)	HCOOH (mol/m ³)	HCHO (mol/m ³)	CH ₃ OH (mol/m ³)	CH ₄ (mol/m ³)	H ₂ (mol/m ³)
0	34.002	0.000	0.000	0.000	0.000	0.000
5	21.252	0.001	8.274	2.252	1.249	10.247
10	15.699	0.001	11.834	4.274	1.903	16.407
25	9.080	0.001	13.723	7.324	3.411	24.438
50	7.760	0.001	8.608	9.685	8.461	31.084
100	6.812	0.001	2.925	8.129	18.479	42.805

			Solution)			
Mean Residence Time (sec)	CO ₂ (mol/m ³)	HCOOH (mol/m ³)	HCHO (mol/m ³)	CH ₃ OH (mol/m ³)	CH ₄ (mol/m ³)	H ₂ (mol/m ³)
0	992.4221	0.0000	0.0000	0.0000	0.0000	0.0000
5	907.4900	0.0050	54.1883	14.1870	9.8124	0.6087
10	868.2290	0.0030	74.7393	26.8260	14.6870	1.0362
25	830.4473	0.0025	86.5790	42.7240	27.3732	1.3414
50	820.2099	0.0014	36.5331	63.8118	58.3329	1.9462
100	811.1485	0.0008	20.4006	34.1559	97.3110	2.8499

Table E-4. Experimental Data (20V Voltage, 500µm Spacer, Ionic Liquid Solution)

Table E-5. Experimental Data (22.5V Voltage, 500µm Spacer, Ionic Liquid Solution)

Mean Residence Time (sec)	CO ₂ (mol/m ³)	HCOOH (mol/m ³)	HCHO (mol/m ³)	CH ₃ OH (mol/m ³)	CH ₄ (mol/m ³)	H ₂ (mol/m ³)
0	992.4221	0.0000	0.0000	0.0000	0.0000	0.0000
5	900.2047	0.0060	56.2444	15.8152	11.1959	0.7291
10	858.4316	0.0040	76.3691	29.0865	16.0583	1.1206
25	818.0297	0.0030	89.3663	44.5990	28.8107	1.5086
50	813.4475	0.0020	39.0037	66.6887	59.9853	2.0543
100	800.6787	0.0011	25.6337	40.3184	104.9928	2.9614

Table E-6. Experimental Data (20V Voltage, 200µm Spacer, Ionic Liquid Solution)

Mean Residence Time (sec)	CO ₂ (mol/m ³)	HCOOH (mol/m ³)	HCHO (mol/m ³)	CH ₃ OH (mol/m ³)	CH ₄ (mol/m ³)	H ₂ (mol/m ³)
0	992.4221	0.0000	0.0000	0.0000	0.0000	0.0000
5	913.8848	0.0052	53.4999	14.5629	9.9393	0.6144
10	860.9288	0.0035	75.1459	26.2416	14.3752	1.0884
25	834.0092	0.0024	84.8799	43.3466	27.3603	1.4120
50	827.1198	0.0017	35.8664	63.1930	58.0482	1.9987
100	809.0296	0.0009	21.7040	33.5893	97.5038	2.9013