Microreactor Engineering

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Microscale-based Corona Reactor for CO_2 Reduction

In affiliation with:

MBI

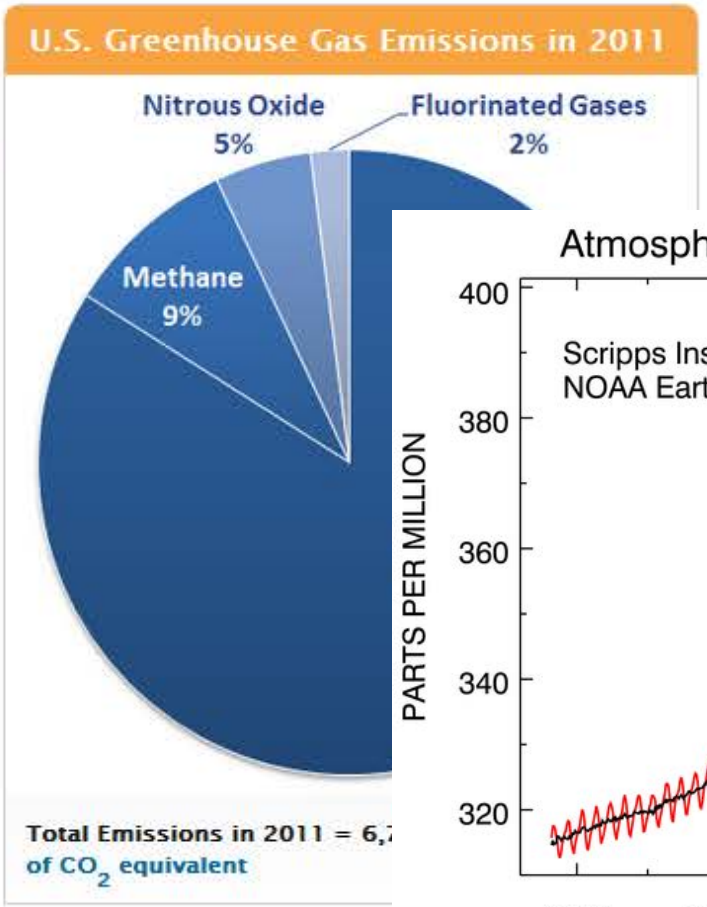
Microproducts Breakthrough Institute

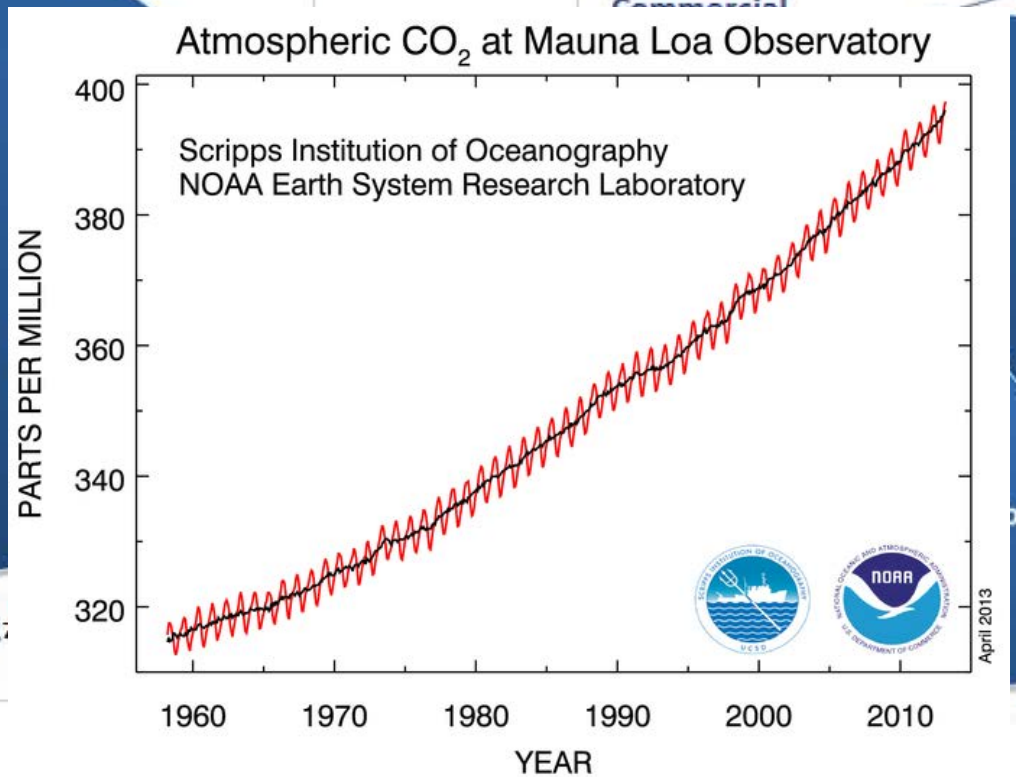
PTT-LOA

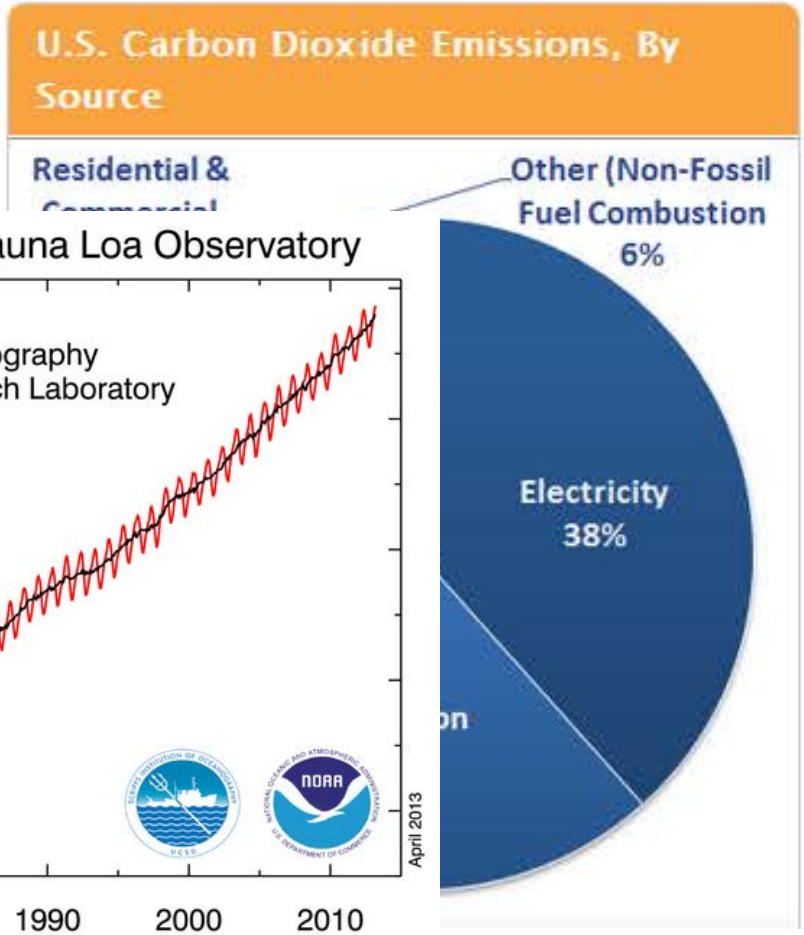
PTT – Laboratory Of America

Description of the Problem

- **Global Warming**







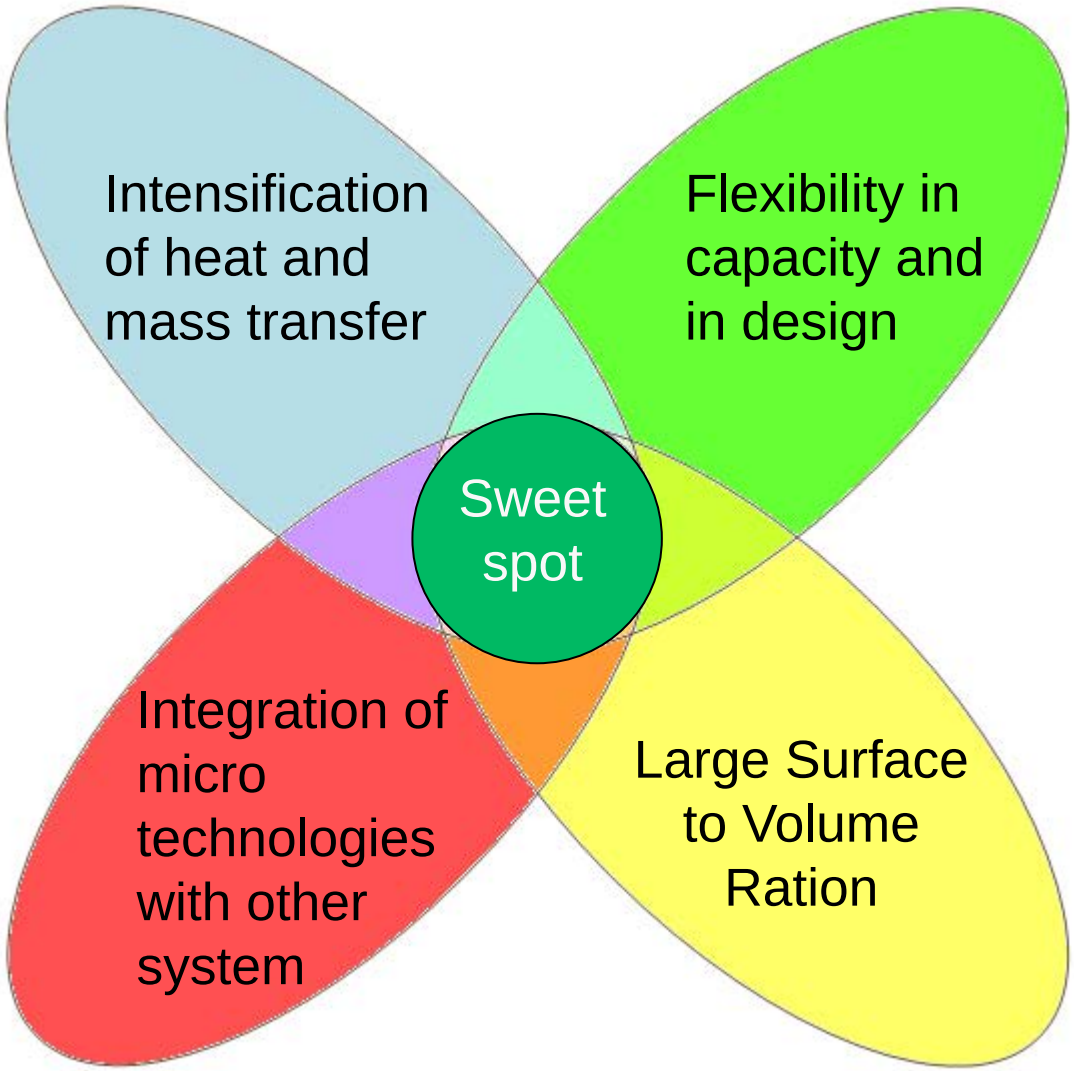
Description of the Problem

- **CO_2 Utilization and Conversion**
  - **Motivations:**
    - Renewable, cheap resource and reduced liability to carbon taxes
    - Nontoxic feedstock
    - Open a new avenue to resource utilization
    - Have a positive impact on global carbon balance
    - Stimulate related industrial processes
  - **Method:**
    - Physical (extraction)
    - Chemical (synthesis, reduction)

Why Microscale-based Technology

- **Microtechnology**
  - **Definitions:**
    - Operation is based on the scale of 1-100 microns
    - Internal structures range from sub-micrometer to sub-millimeter level
  - **Fundamental Advantages:**
    - From fundamental phenomena
    - From parallel architecture
    - From commercial application
    - In the area of safety and security

Why Microscale-based Technology



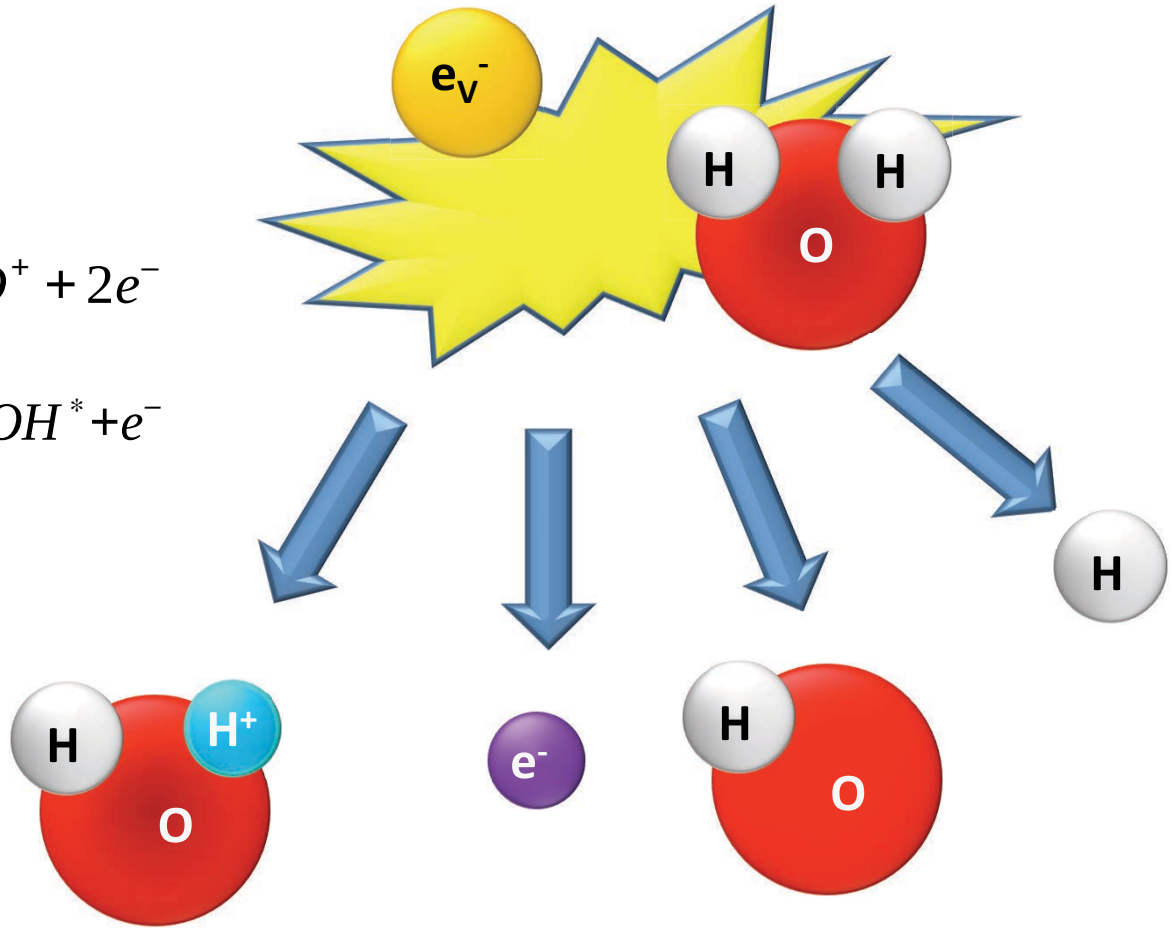
Reaction Chemistry

Mechanism

Step 1:

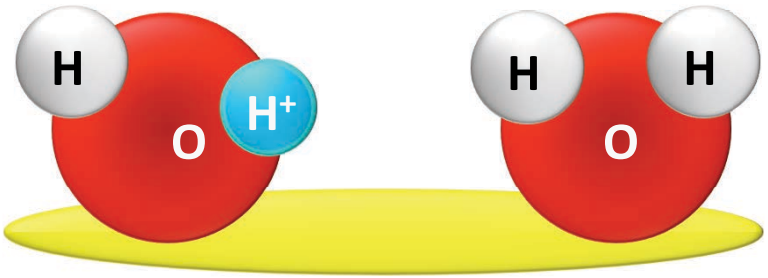
$$e_V^- + H_2O \xrightarrow{k_1} H_2O^+ + 2e^-$$

$$e_V^- + H_2O \xrightarrow{k_2} H^* + OH^* + e^-$$



Reaction Chemistry

- **Step 2:**



$$H_2O^+ + H_2O \xrightarrow{k_3} H_3O^+ + OH^*$$

$$2OH^* \xrightarrow{k_4} H_2O_2$$

$$H^* + OH^* \xrightarrow{k_5} H_2O$$

$$H_2O_2 + e^- \xrightarrow{k_6} OH^* + OH^-$$

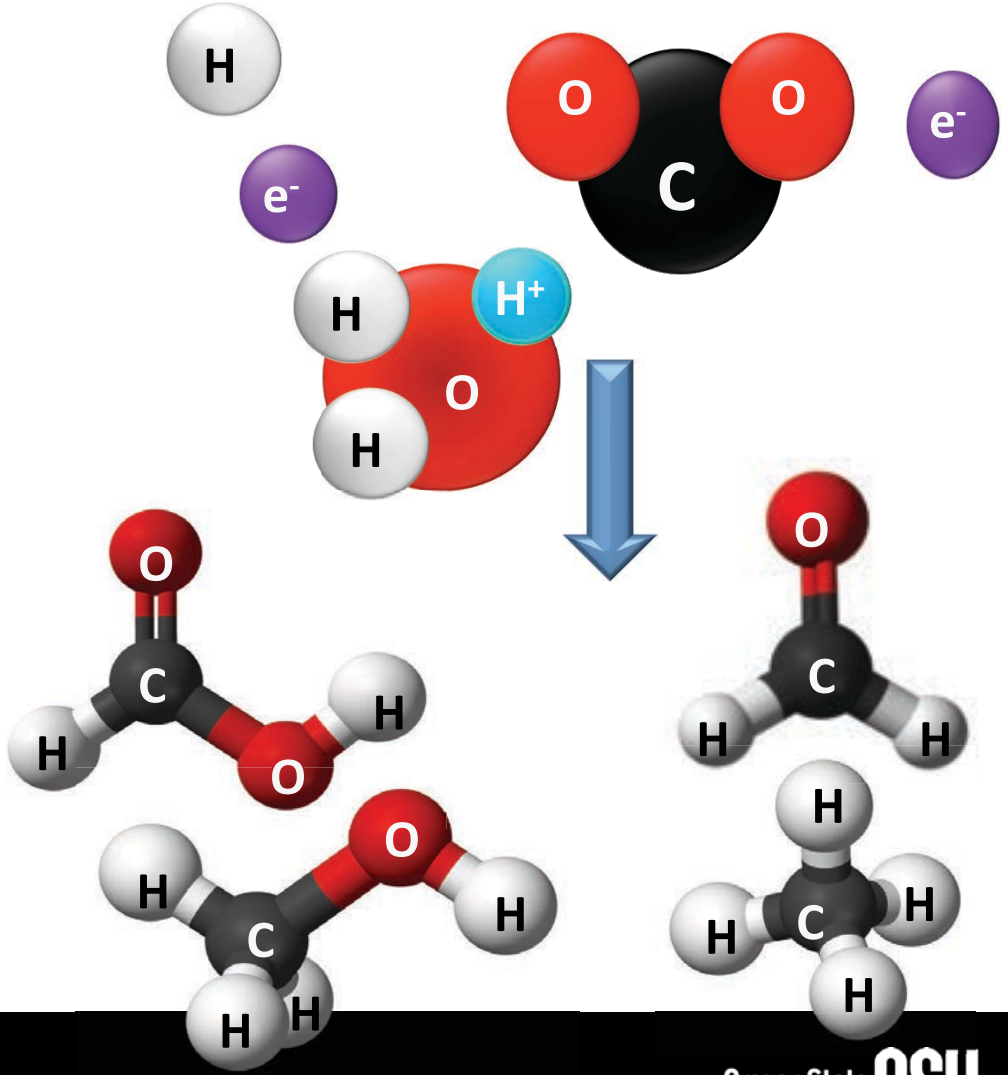
$$H_3O^+ + OH^- \xrightarrow{k_7} 2H_2O$$

$$CO_2 + H_2O \underset{k_{-8}}{\overset{k_8}{\longleftrightarrow}} H_2CO_3$$

$$H_2CO_3 \underset{k_{-9}}{\overset{k_9}{\longleftrightarrow}} 2H^+ + CO_3^{2-}$$

Reaction Chemistry

- **Step 3 (DI-water as solvent) :**



$$H_3O^+ + e^- \xrightarrow{k_{10}} H^* + H_2O$$

$$2H^* \xrightarrow{k_{11}} H_2$$

$$CO_2 + e^- \xrightarrow{k_{12}} O = C^* - O^-$$

$$\boxed{O = C^* - O^- + H_3O^+ \xrightarrow{k_{13}} O = C^* - OH + H_2O}$$

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

$$O = CH - OH + e^- \xrightarrow{k_{15}} OH - HC^* - O^-$$

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

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

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

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

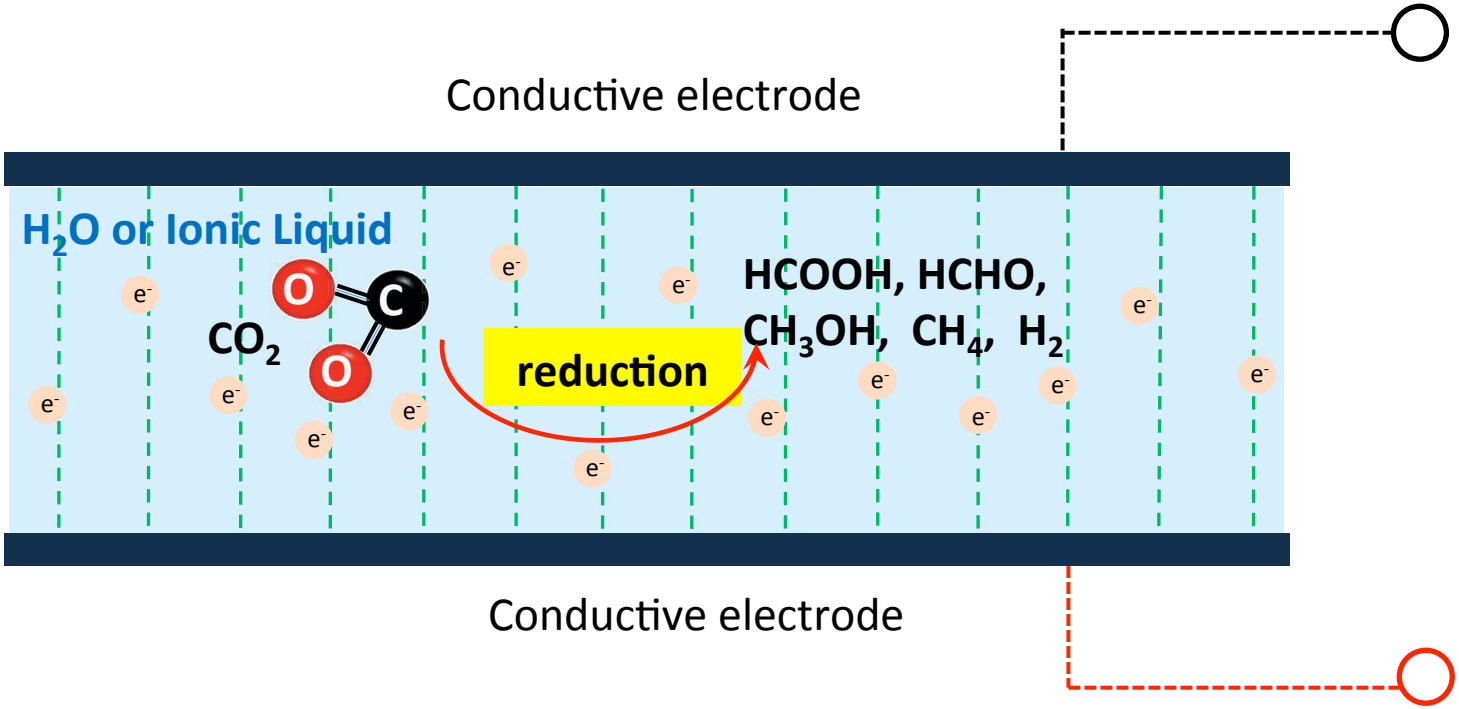
$$HC^*H - OH + H^* \xrightarrow{k_{22}} CH_3OH$$

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

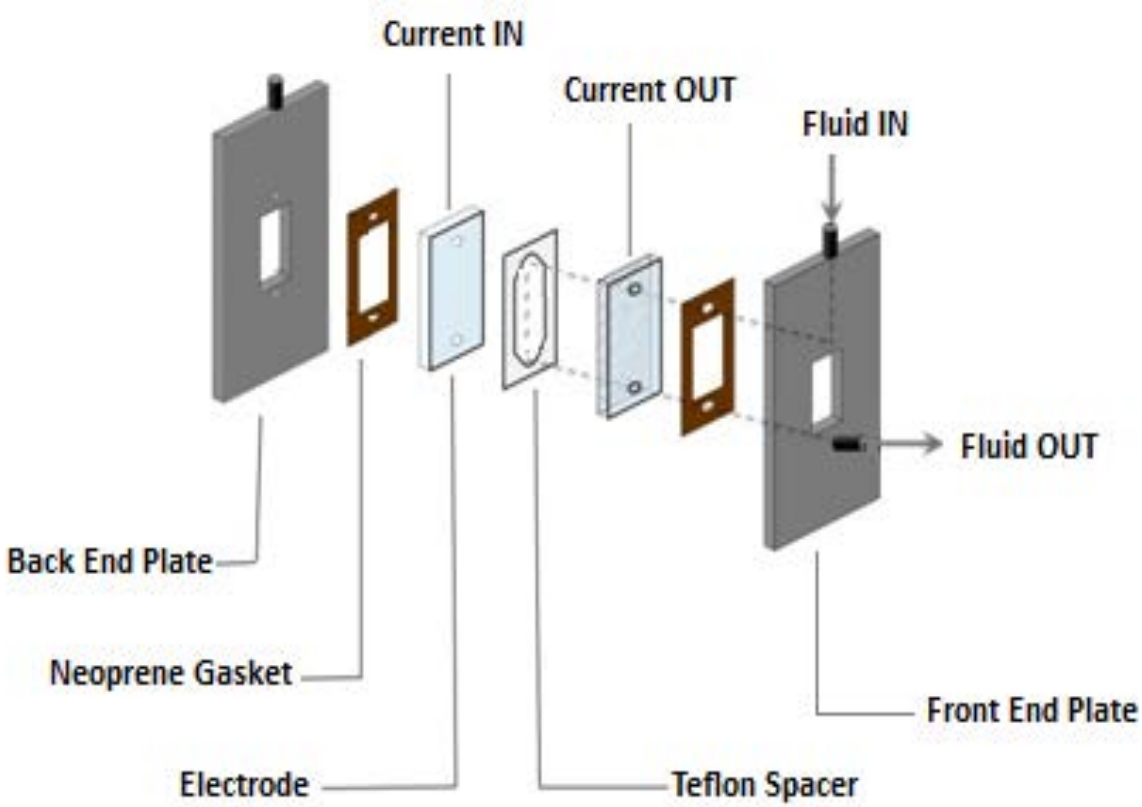
$$C^*H_3 + H^* \xrightarrow{k_{24}} CH_4$$

Corona Microreactor

- **Process of Electrochemical Reduction of CO_2**

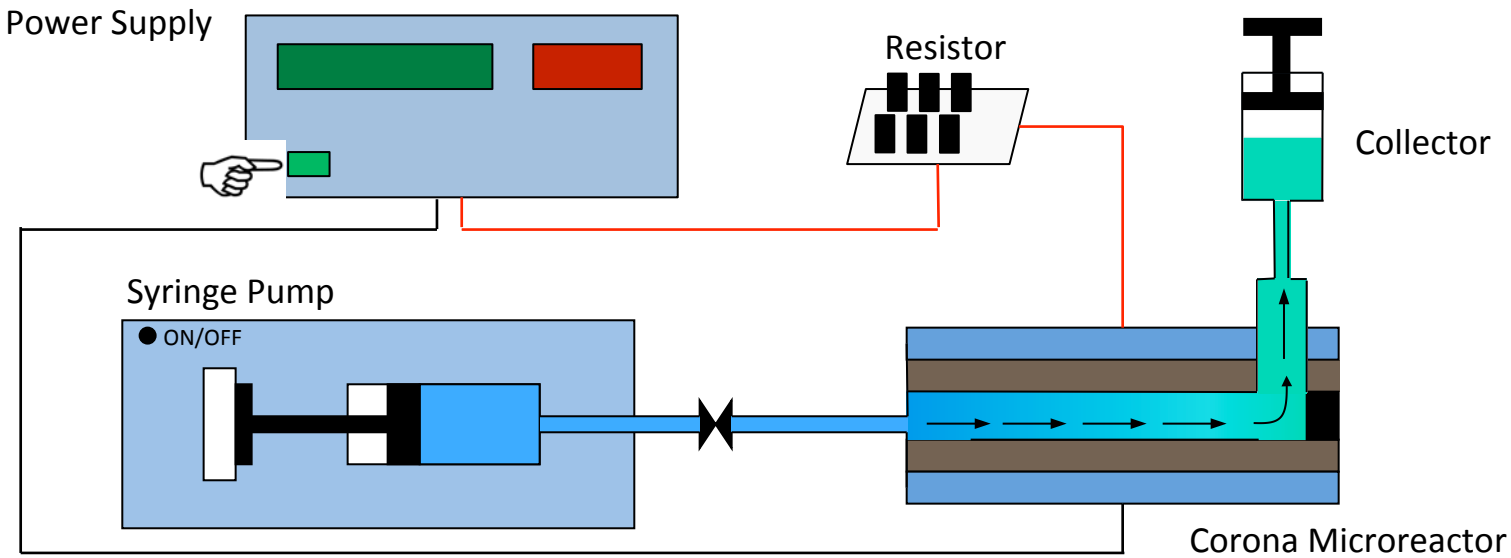


Corona Microreactor

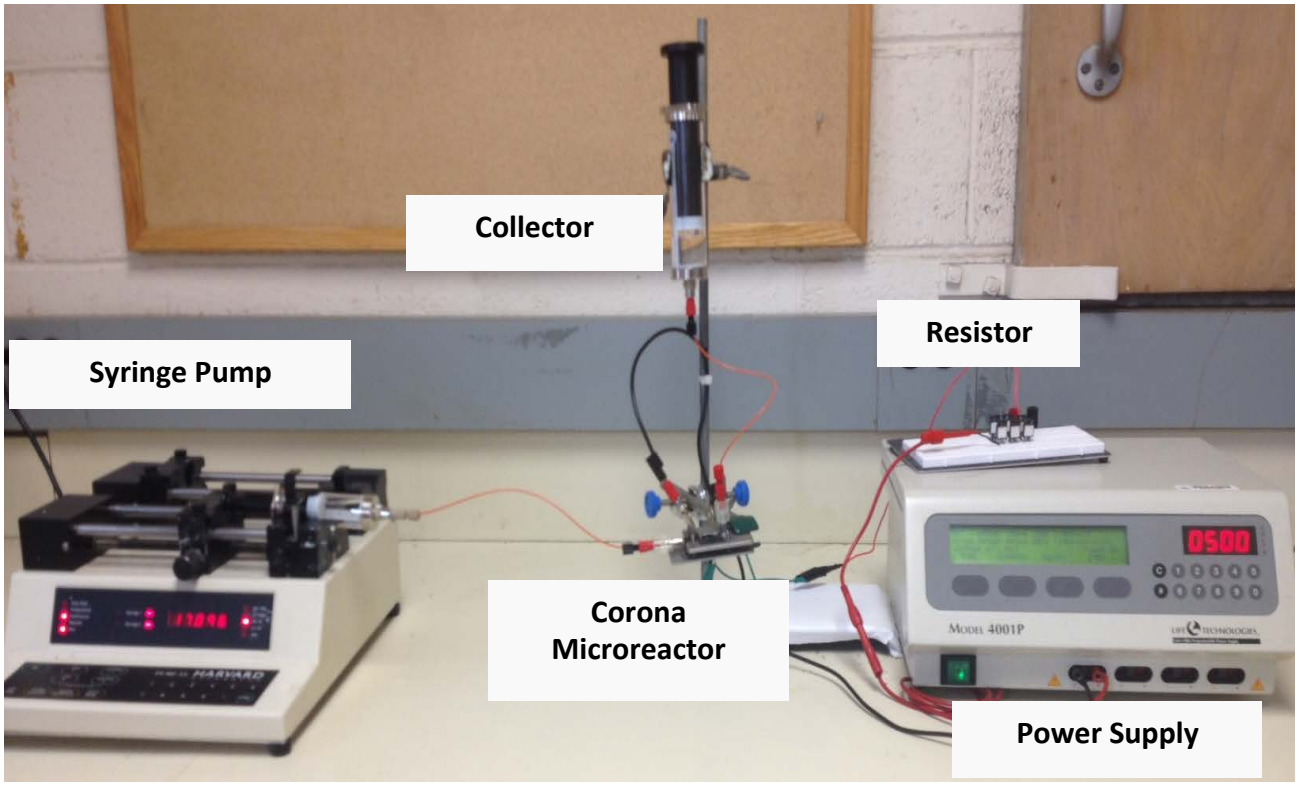


Corona Microreactor

Microreactor Test-Loop

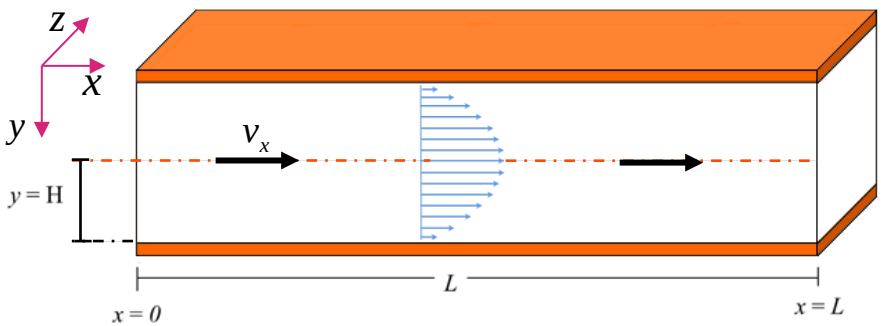


Microreactor Test-Loop



Mathematical Model

Momentum Balance



Assumptions:

1. Newtonian, laminar, isothermal and incompressible fluid
2. Steady-state condition
3. No velocity in *y* and *z* direction
4. No velocity change along *z* direction
5. Neglect gravity

Continuity equation:

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

Navier-Stokes equations:

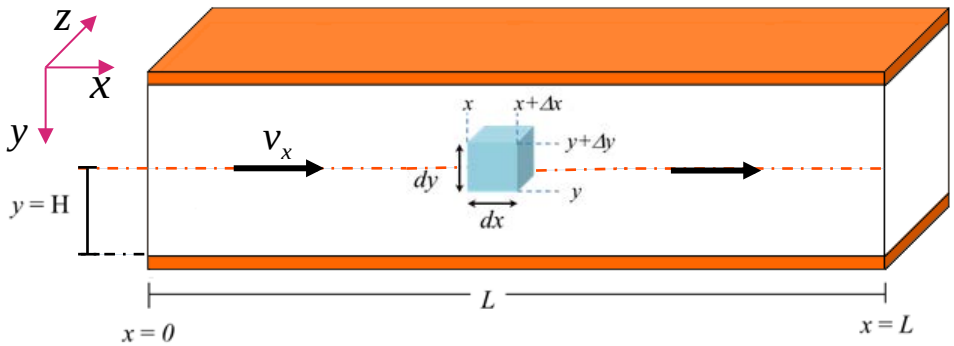
$$\rho\left(\frac{\partial \upsilon}{\partial t} + \mathrm{v}\cdot\nabla\mathrm{v}\right) = -\nabla p + \nabla\cdot\mathrm{T} + F$$

Boundary conditions:

$$\left.\begin{array}{ll} @\,x=0, \quad P=P_0 & @\,x=L, \quad P=P_L \\ @\,y=0, \quad \dfrac{\partial v_x}{\partial y}=0 & @\,y=H, \quad v_x=0 \end{array}\right\} \Rightarrow \boxed{v_x = \frac{P_L - P_0}{2\mu L}\left(y^2 - H^2\right)}$$

Mathematical Model

Material Balance



Assumptions:

1. No convection in *y* direction
2. No convection in *z* direction
3. Steady state process
4. Dilute solution

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

Mass Balance equations:

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

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

Boundary conditions:

$$@\, x = 0, \quad \frac{\partial C_i(0,y)}{\partial x} = 0 \qquad @\, x = L, \quad \frac{\partial C_i(L,y)}{\partial x} = 0$$

$$@\, y = 0, \quad \frac{\partial C_i(x,0)}{\partial y} = 0 \qquad @\, y = H, \quad \frac{\partial C_i(x,H)}{\partial y} = 0$$

Mathematical Model

- **Assumptions:**

1. Reduction in the corona rector is completed via e^-, H_3O^+ and H^* attack on CO_2;
2. The concentration of e^- is constant at steady state;
3. Concentrations of all radicals and intermediates are constant at steady state;
4. Concentrations of H_2O^+ and e^- are equal;
5. Almost all the H_3O^+ is used to produce H^*;
6. Almost all the CO_2 is used to produce hydro carbonates instead of carbonic acid.

- **Reaction Rates in the bulk of the Reactor**

$$r_{CO_2} = -k_{12}[CO_2][e^-] = -k_{12}[CO_2]\frac{k_1 V}{k_3}$$

$$r_{HCOOH} = k_{12}[CO_2][e^-] - k_{15}[HCOOH][e^-] = \left(k_{12}[CO_2] - k_{15}[HCOOH]\right)\frac{k_1 V}{k_3}$$

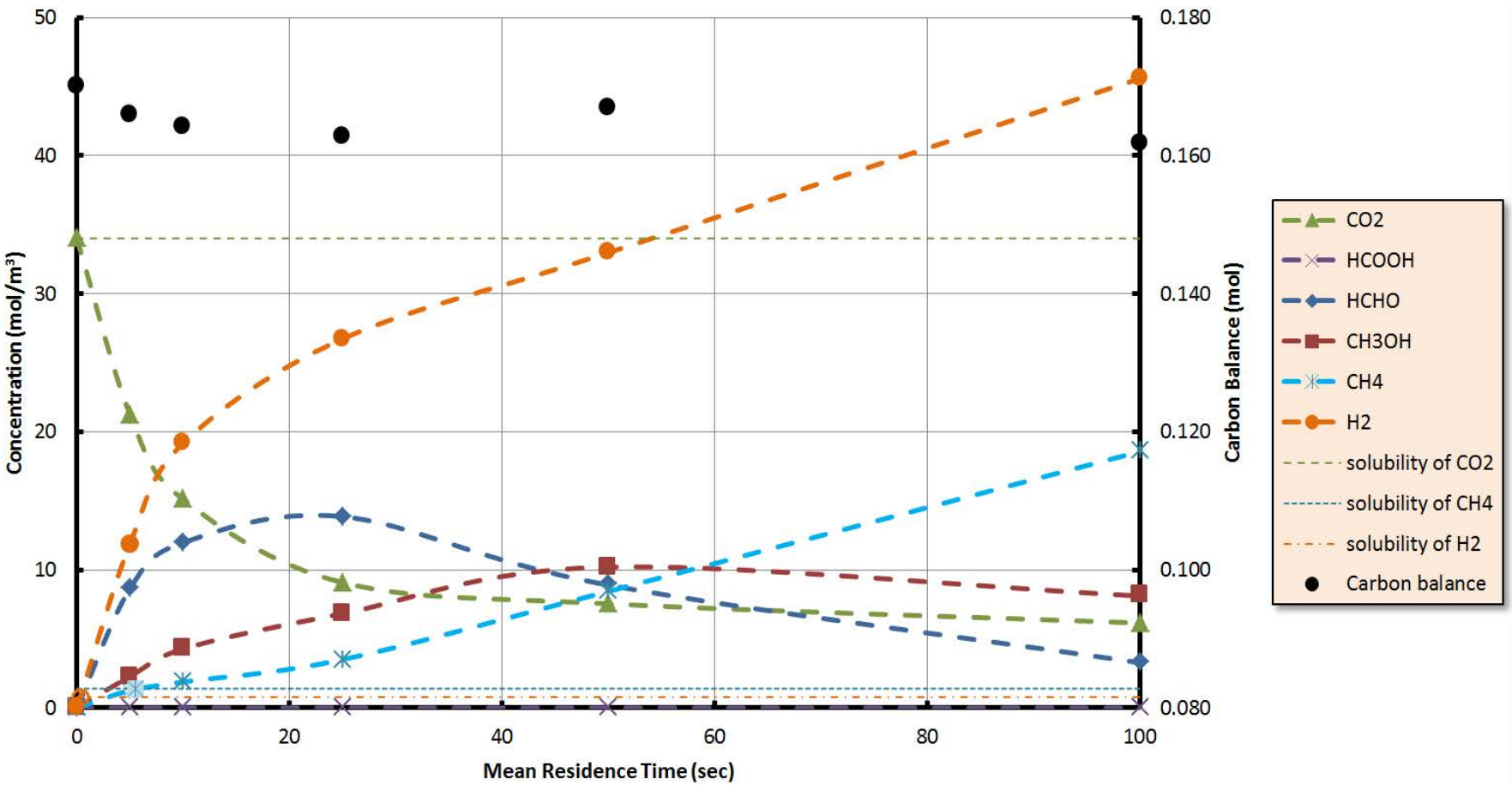
$$r_{HCHO} = k_{15}[HCOOH][e^-] - k_{20}[HCHO][e^-] = \left(k_{15}[HCOOH] - k_{20}[HCHO]\right)\frac{k_1 V}{k_3}$$

$$r_{CH_3OH} = k_{20}[HCHO][e^-] - k_{23}[H^*][CH_3OH] = k_{20}\frac{k_1 V}{k_3}[HCHO] - k_{23}[CH_3OH]\frac{\sqrt{k_4(k_1+k_2)V[H_2O]}}{k_5}$$

$$r_{CH_4} = k_{23}[H^*][CH_3OH] = k_{23}[CH_3OH]\frac{\sqrt{k_4(k_1+k_2)V[H_2O]}}{k_5}$$

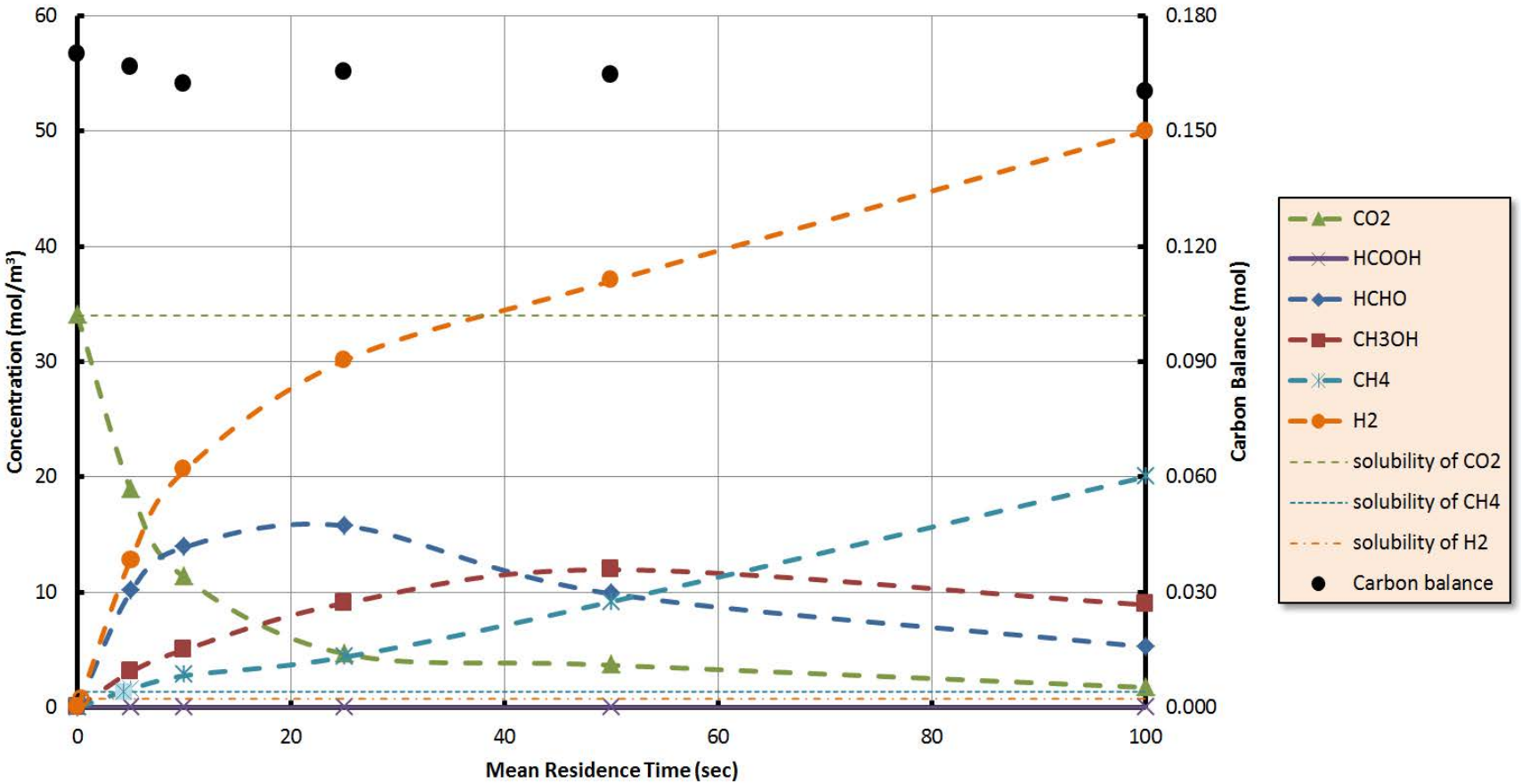
Experimental Data

- 20 [V] Across Reactor, 500 [µm] Spacer in Aqueous Solution



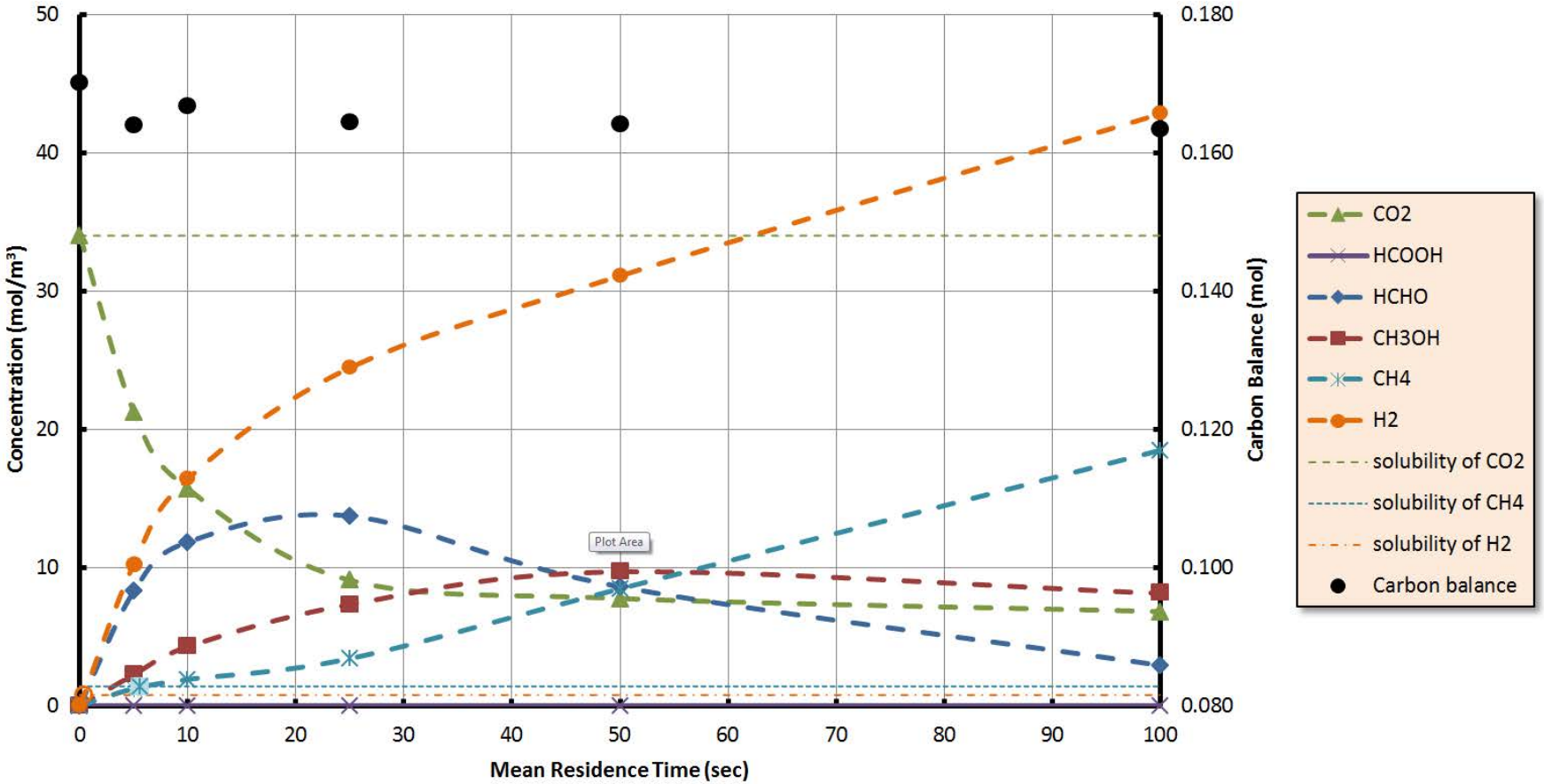
Experimental Data

- 22.5 [V] Across Reactor, 500 [µm] Spacer in Aqueous Solution



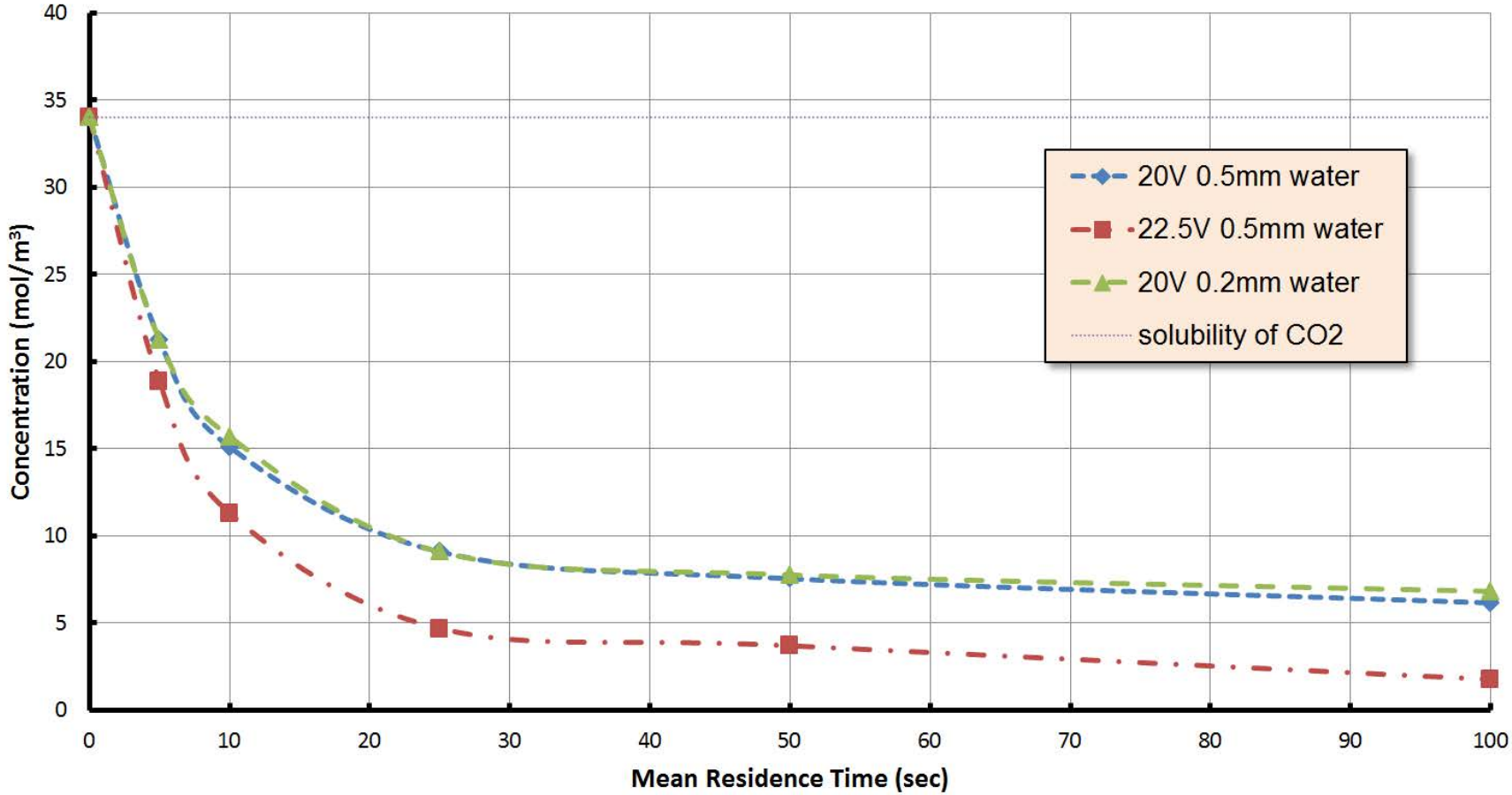
Experimental Data

- 20 [V] Across Reactor, 200 [µm] Spacer in Aqueous Solution

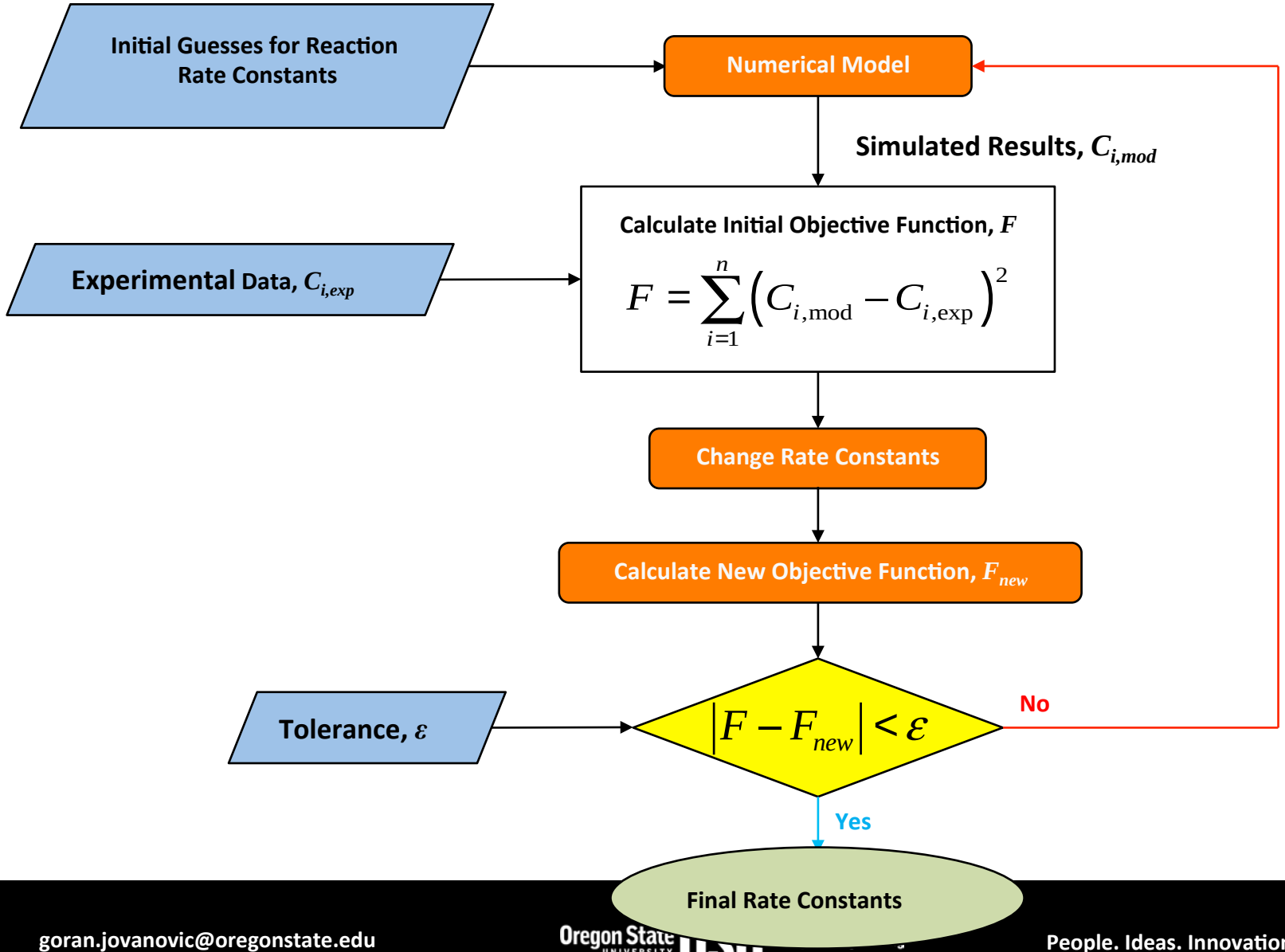


Experimental Data

- CO_2 Data in Aqueous Solution



Determination of Reaction Rate Constants



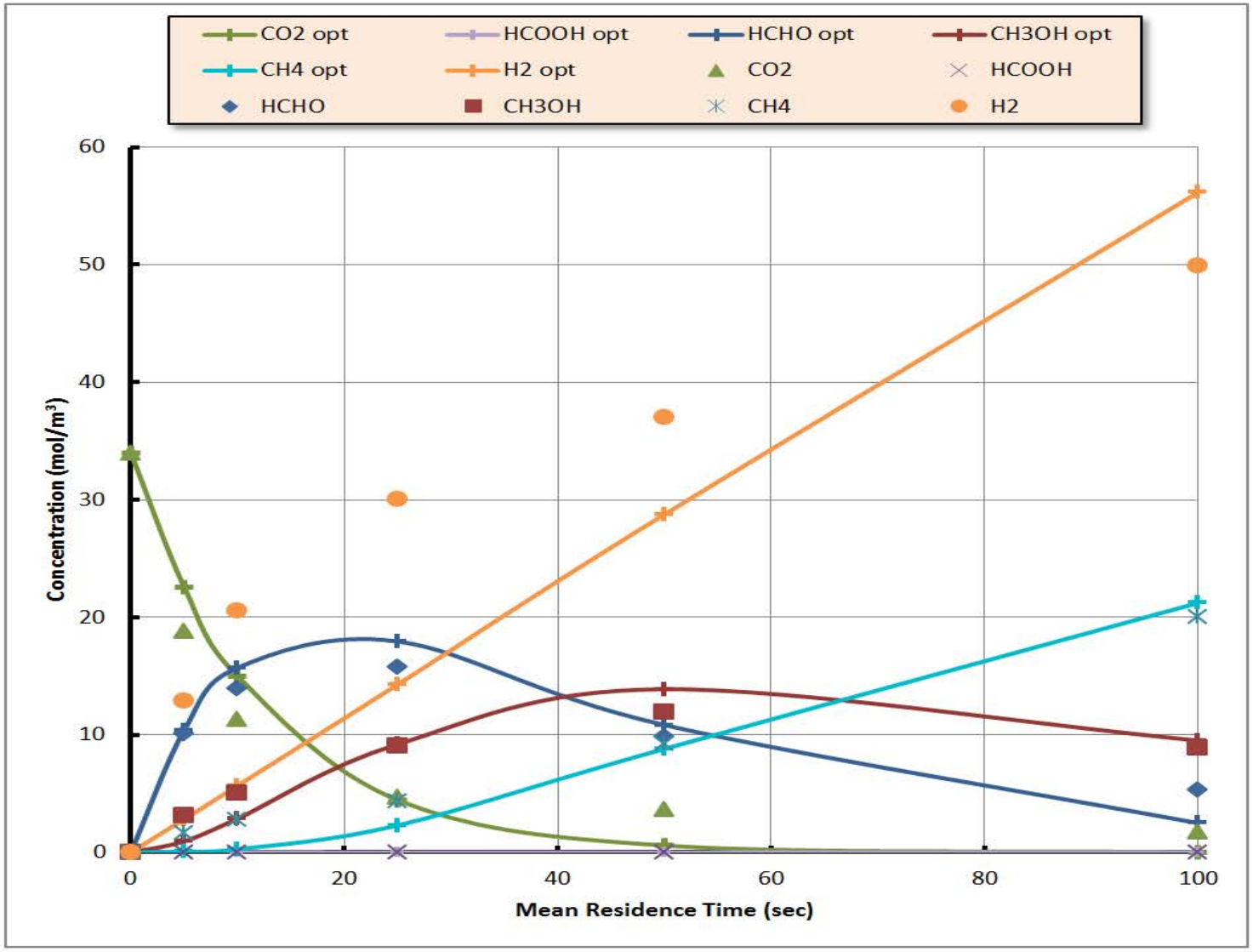
Determination of Reaction Rate Constants

- **Reaction Rate Constants**

Reaction Rate Constants	Aqueous Solution	Ionic Liquid Solution
Production Rate Constant of H_2 [$m^3/(mol\cdot s)$], k_{11}	3.02×10^{-2}	1.65×10^{-5}
Consumption Rate Constant of CO_2 [$m^3/(mol\cdot s)$], k_{12}	2.70×10^{-3}	6.40×10^{-3}
Production Rate Constant of HCHO [$m^3/(mol\cdot s)$], k_{15}	$9.81\text{x}10^{-1}$	$1.48\text{x}10^{0}$
Production Rate Constant of CH_3OH [$m^3/(mol\cdot s)$], k_{20}	9.81×10^{-4}	8.40×10^{-4}
Production Rate Constant of CH_4 [$m^3/(mol\cdot s)$], k_{23}	4.80×10^{-3}	1.90×10^{-3}
Production Rate Constant of H* [1], $K=((k_1+k_2)\cdot k_4)^{0.5}/k_5$	3.30×10^{-3}	2.19×10^{-2}

Determination of Reaction Rate Constants

- **Optimization Result in Aqueous Solution**



References

1) Young Ku, Wan-Hui Lee, Wen-Yu Wang. "Photocatalytic reduction of carbonate in aqueous solution by UV/TiO_2 process." *Journal of Molecular Catalysis A: Chemical.* 212.(2004): 191-196.Print.
2) Sasirekha, Natarajan, Sheikh John Sardhar Basha, and Kannan Shanthi. "Photocatalytic performance of Ru doped anatase mounted on silica for reduction of carbon dioxide." *Applied Catalysis B: Environmental*. 62. (2006): 169-180. Print.
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People. Ideas. Innovation.

Thank you for your attention!

Special thanks to Mr. Yu Miao from OSU for the help in developing this material.