A Kinetic Model for the Reduction of CO₂ in a Corona Plasma Discharge for Syngas production

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Outline

- 4CU & Plasmolytic reduction
- What is a Plasma?
- CO$_2$ Plasma Model
  - Reaction Scheme
  - Modelling Chart
  - Results
4CU Programme Grant

- 4 year, £5.7m project funded by EPSRC started September 2012
- Main aim is the **sustainable conversion of CO$_2$ to fuel**
Aim: Activation of CO₂ using non-thermal plasma technology to produce Syngas

- Study of reactor geometries and impact on process parameters on dissociation of CO₂ molecules
- Development of in-situ spectroscopy techniques to evaluate reactions mechanism
- Development of novel electrodes to generate plasma at lower voltage
- Development of a kinetic model to further advance experimental work
What is a Plasma?

“A plasma is a quasineutral gas of charged and neutral particles which exhibits collective behavior”

Francis F. Chen

i.e. the fourth state of matter!

Plasma has many applications

• Fusion research
• Semiconductor industry
• Lighting industry
• Chemical industry
• Gas cleaning
• …..
The most common types of plasma are:

- Inductively coupled plasmas (ICP)
- Capacitively coupled plasmas (CCP)
  - Corona discharges
    (already used industrially for large scale gas treatment)

(From http://www.plasmacenter.pl/corona.htm)
A plasma discharge consists of:

- Electrons
- Neutral particles
- Excited species
- Ions (positive and negative)
Challenges in Plasma Modelling

The broad range of characteristic time scales for the different interactions between components in a plasma discharge creates numerical difficulties.

- Plasma chemistry data is very hard to find or not exist at all...when available, come in different formats!
- Stiffness in space (charge separation needs to be resolved).
- Stiffness in time (different time scales)
- Large number of degrees of freedom (many species)
- Strong couplings between electron energy and electromagnetic fields, transport of charged species and electromagnetic fields, etc.

Hence, plasma processes are considered unpredictable and extremely difficult to model...

However, this is changing with the availability of new commercial software.
Potential benefits of non-thermal plasma

- Non-equilibrium, where temperature of electron higher than gas temperature
- High electron temperature
- Low gas temperature
- Low currents
- Selective tool (potential for greater efficiency)

“COLD” PLASMA
Why coronas for CO$_2$ dissociation?

- Non-thermal.
- CO$_2$ molecule has resonant vibrational energy levels (V-V relax high, V-T relax low).
- Corona discharges can be tuned to the resonant frequencies of CO$_2$ molecules.
- Despite transient phenomena, coronas are, in good approximation, well behaved...Predictable!
- Easy to design, build, operate and couple to diagnostics systems
CO₂ decomposition in a plasma

This is a truly multiphysics problem, because it involves:

- Electron dynamics (Boltzmann equation, energy equation)
- Electron/heavy species mass transport equations
- Fluid dynamics (flow equations)
- Heat transfer
- Ion transport
- Reaction engineering (chemical reactions)
- Electrodynamics
- Interaction with external circuit (power supply)

**Comsol Multiphysics**
chosen because it has a dedicated plasma module that integrates all these physics modes into a single computational environment!
Creating a kinetic model for a CO$_2$ plasma discharge

Widely thought of as being almost impossible!
**Reaction scheme**

**Initial species:** $e + \text{CO}_2 \rightarrow \text{CO}, \text{O}, \text{O}_2, \text{O}_3, \text{C}, \text{O}^-, \text{O}_2^-, \text{CO}_3^-, \text{CO}_4^-, \text{O}_2^*, \text{O}^*, \text{O}_2^*$

**Electron impact dissociation**
- $e + \text{CO}_2 \rightarrow \text{CO} + \text{O} + e$
- $e + \text{O}_2 \rightarrow \text{O} + \text{O} + e$
- $e + \text{O}_3 \rightarrow \text{O} + \text{O}_2 + e$
- $e + \text{CO} \rightarrow \text{C} + \text{O} + e$

**Ion-molecule reactions**
- $\text{O}^- + \text{CO}_2 + \text{CO}_2 \rightarrow \text{CO}_3^- + \text{CO}_2$
- $\text{O}_2^- + \text{CO}_2 + \text{CO}_2 \rightarrow \text{CO}_4^- + \text{CO}_2$

**Electron attachment**
- $e + \text{CO}_2 \rightarrow \text{O}^- + \text{CO}$
- $e + \text{O}_2 \rightarrow \text{O}^- + \text{O}$
- $e + \text{O}_3 \rightarrow \text{O}^- + \text{O}_2$
- $e + \text{O}_3 \rightarrow \text{O}_2^- + \text{O}$
- $e + \text{O}_2 + \text{O}_2 \rightarrow \text{O}_2^- + \text{O}_2$

**Heavy – heavy reactions**
- $\text{O} + \text{O}_2 + \text{O}_2 \rightarrow \text{O}_3 + \text{O}_2$
- $\text{O} + \text{O}_2 + \text{CO}_2 \rightarrow \text{O}_3 + \text{CO}_2$
- $\text{O} + \text{O} + \text{CO}_2 \rightarrow \text{O}_2 + \text{CO}_2$
- $\text{O} + \text{O} + \text{CO}_2 \rightarrow \text{O}_2 + \text{CO}_2$
- $\text{O} + \text{O} + \text{CO}_2 \rightarrow \text{O}_2 + \text{CO}_2$
- $\text{O}_3 + \text{O}_2(1\text{D}_g) \rightarrow \text{O}_2 + \text{O}_2 + \text{O}$
- $\text{O} + \text{CO} + \text{CO}_2 \rightarrow \text{CO}_2 + \text{CO}_2$
- $\text{C} + \text{CO} + \text{CO}_2 \rightarrow \text{C}_2\text{O} + \text{CO}_2$
- $\text{O} + \text{C}_2\text{O} \rightarrow \text{CO} + \text{CO}$
Solving the 0D model (no spatial dependencies)

- Begin with collision data, and use Boltzmann solver to find electron energy distribution (EEDF)
- Calculate reaction rates for kinetic model using COMSOL
- Obtain species evolution
A spatially resolved model

- Kinetic model can be used with fluid dynamics and electrostatics in COMSOL for a 1D model incorporating reactor geometry
- Spatial features are coupled to kinetic model
- EEDF can be determined experimentally and fed back into rate calculator
An Electrical Model

- Using PSpice the reactor can be modeled as an electrical circuit based on data from the spatially resolved kinetic model giving power consumption.

Modelling chart

Collision Data
  → Boltzmann Solver
    → EEDF
      ↓ Rates
          ↓ Rate Calculator
              ↓ Kinetic Model
                  ↓ Operating Conditions
                      ↓ Electron Energy Equation
                          ↓ Species Evolution
                              ↓ Flow Regime
                                  ↓ Potential Distribution
                                      ↓ Temperature Field
                                          ↓ Power Usage
                                              ↓ Electrical Model

The University Of Sheffield
Modelling chart - Summary

0D Model
Strongly coupled 0D variables
Spatially dependent model – also coupled
An Electrical Model

Collision Data
Boltzmann Solver
EEDF
Rate Calculator
Rates
Electron energy Equation
Operating Conditions

Electrical Model
Power Usage

Temperature Field
Species Evolution
Flow Regime
Potential Distribution

Kinetic Model

4CU Foreseeing a future using CO₂
1) Species Continuity Equation
Describes conservation of the plasma species, j

\[ \frac{\partial n_j}{\partial t} + \nabla \Gamma_j = \sum_l R_{j,l} \]

Accumulation  Flux term  Reaction term

j = electrons, ions, neutrals
1) **Species Continuity Equation**
Describes conservation of the plasma species, $j$

\[
\frac{\partial n_j}{\partial t} + \nabla \cdot \Gamma_j = \sum_l R_{j,l}
\]

$j = \text{electrons, ions, neutrals}$

2) **Drift Diffusion Approximation**
Describes movement of the plasma species, $j$

\[
\Gamma_j = \pm n_j \mu_j E - D_j n_j
\]

Drift Term – Depends on charge of species, and electric field
Diffusion Term – Introduces diffusivity of species
Kinetic Model

1) Species Continuity Equation
Describes conservation of the plasma species, $j$

$$\frac{\partial n_j}{\partial t} + \nabla \cdot \Gamma_j = \sum_l R_{j,l}$$

$j = \text{electrons, ions, neutrals}$

2) Drift Diffusion Approximation
Describes movement of the plasma species, $j$

$$\Gamma_j = \pm n_j \mu_j E - D_j n_j$$

3) Electron Energy Equation
Describes distribution of electron energies

$$\frac{\partial (n_e \mathcal{E})}{\partial t} + \nabla \cdot \left( \frac{5}{3} \mathcal{E} \Gamma_e - \frac{5}{3} n_e D_e \nabla \mathcal{E} \right) = -\Gamma_e \nabla \mathcal{E} - Q_{e-N}$$

Electron energy flux
Electron “heating” due to electric field
Collisional energy loss
Kinetic Model

1) Species Continuity Equation
Describes conservation of the plasma species, j

$$\frac{\partial n_j}{\partial t} + \nabla \cdot \Gamma_j = \sum_l R_{j,l}$$

j = electrons, ions, neutrals

2) Drift Diffusion Approximation
Describes movement of the plasma species, j

$$\Gamma_j = \pm n_j \mu_j E - D_j n_j$$

3) Electron Energy Equation
Describes distribution of electron energies

$$\frac{\partial (n_e \varepsilon)}{\partial t} + \nabla \cdot \left( \frac{5}{3} \varepsilon \Gamma_e - \frac{5}{3} n_e D_e \nabla \varepsilon \right) = -\Gamma_e \nabla \varepsilon - Q_{e-N}$$

4) Poisson Equation
The effect of charged species on the electric potential

$$\varepsilon_0 \nabla \cdot \vec{E} = \sum_j q_j n_j$$

Dielectric constant
Charge distribution
Results – CO production

$\text{CO}_2$ splits into CO, $\text{O}_3$, $\text{CO}_3^{-}$, $\text{O}_2$, $\text{O}$, $\text{CO}_4^{-}$...

But, CO dominates!

Conditions:
$\text{Te}=2.6 \text{ eV}, \text{Tg}=300 \text{K}$
Results - Effect of \( \text{CO}_2 / \text{O}_2 \) ratio

- \( \text{CO} \) concentration increases with increasing \% \( \text{CO}_2 \).
- \( \text{O}_3 \) concentration decreases with increasing \% \( \text{CO}_2 \).
- \( \text{C} \) concentration increases with increasing \% \( \text{CO}_2 \).
- \( \text{O} \) concentration decreases with increasing \% \( \text{CO}_2 \).
Results - Pure H\textsubscript{2}O model

H\textsubscript{2}O splits into H\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, HO\textsubscript{2}, OH and H
But, H\textsubscript{2} and O\textsubscript{2} species dominate!
Conclusions

• Plasma corona discharges are suitable for CO$_2$ dissociation. For Te=2.6 eV, Tg=300 K, 2 Atm conditions, $\approx 48\%$ conversion into CO can be achieved.

• Excitation of vibrational modes in CO$_2$ molecules allow for selective transfer of energy. Hence, potential for greater efficiency than thermal plasma.

• Plasma simulation with new commercial software makes easier what was terribly difficult just few years ago.

• Alternative routes to syngas production:
  • CO$_2$ dissociation with plasma corona reactors + parallel H$_2$O dissociation (also has resonant vibrational modes)
  • CO$_2$ + H$_2$O together ... Future work!
Acknowledgements

EPSRC
Engineering and Physical Sciences Research Council

The University Of Sheffield.

UCL

Queen’s University Belfast

The University of Manchester

4CU
Foreseeing a future using CO₂

http://4cu.org.uk
Additional slides
Available codes for plasma simulation

CFD-ACE+:
- general PDE solver
- plasma physics module available
- ESI Group (http://www.esi-group.com/)

ANSYS Fluent:
- general fluid dynamics solver
- applicable to low pressure CVD simulation
- ANSYS Inc. (http://www.ansys.com/)

COMSOL Multiphysics:
- FE (finite element) solver
- ~20 pre-defined application modules from fluid dynamics to mechanics
- plasma module included in version 4.1
- Comsol, Inc. (http://www.comsol.com/)

The wide spread use of plasmas means that modelling software has become commercially available. This opens up possibilities for gaining basic understanding of plasma processes that did not exist until very recently!
Minimum experimental requirements to create plasma
Experimental schematic

H₂O

Vapour System → Plasma Reactor

MFC

CO₂

CG

Current Monitor

Power Supply

HV Probe

Gas Chromatography

Spectroscopy

Products Out

Equipment required for characterisation
Experimental data obtained can then be used to refine model.
Corona discharge reactor

Key Features:
- Coaxial geometry with internal live electrode
- Powered by a pulsed high voltage DC power source
- Quartz windows allowing direct optical access for spectroscopy
What is a Plasma?

“A plasma is a quasineutral gas of charged and neutral particles which exhibits collective behaviour”. Francis F. Chen

i.e. the fourth state of matter!

(Courtesy of DOE Fusion labs, NASA & Steve Albers)