Production of Sustainable aircraft grade Kerosene from water and air powered by Renewable Electricity, through the splitting of CO₂, syngas formation and Fischer-Tropsch synthesis

**Power-to-X: On the development of a KEROGREEN reactor module for sustainable CO production and the challenges in CO₂ plasmolysis and gas separation**

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**DUTCH INSTITUTE FOR FUNDAMENTAL ENERGY RESEARCH, EINDHOVEN, THE NETHERLANDS**

*Trend workshop: “Plasma(-catalysis) in gas conversion processes”*
The KEROGREEN project

Kerogreen aim: Demonstration of the full chain process from renewable, electricity, CO₂ (captured) and H₂O to kerosene.

- Research and optimisation of individual process steps TRL (1-3) → 4
- Integration phase at Karlsruhe Institute of Technology → >1 L per day
- Duration 2018-2022

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Outline

• The KEROGREEN project

• **Plasmolysis of CO₂**
  • Scientific insights of microwave plasma based processes
  • Engineering constraints during process chain integration

• **Oxygen separation**
  • Solid Oxide Electrochemical Cell (SOEC) based approach
  • Potential & Challenges

• Summary
Main project challenges

- System integration of different technologies into one container sized assembly
- Oxygen separation after plasmolysis by SOEC
- Energy and carbon efficiency of the full chain

Main upstream (DIFFER) challenges

- Plasma modeling and optimisation
- Plasma upscaling 1 → 6 kW (2450 → 915 MHz)
- (Material) Requirements for using SOECs as oxygen separator
- SOEC upscaling from 1 W to 1500 W
**FINAL EVENT**

27th September 2022 – 8:45-15:15 hrs
@ KIT, Karlsruhe + remote

Current challenges in **Sustainable Aviation Fuel synthesis**
**Power-to-X enabling technology** combined with **Plasma Technology**

Get an overview of the latest **KEROGREEN results**
Exchange ideas and discuss with **invited speakers**
**On-site visit** to KIT Energy Lab 2.0

>>> Registration: [https://www.kerogreen.eu/249.php](https://www.kerogreen.eu/249.php) <<<
Why \( \text{CO}_2 \) plasmolysis?

\[ \text{CO}_2 \text{ plasmolysis: } 2\text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2 \]

- Input: \( \text{CO}_2 \) + renewable electricity
- Output: \( \text{CO}_2 \), \( \text{CO} \) and \( \text{O}_2 \)
- High efficiencies, …
- Main challenge downstream: \( \text{O}_2 \) separation

DOI: 10.1017/CBO9780511546075
CO₂ plasmolysis in literature

Specific Energy Input ($SEI, E_{\text{Spec}}$)

$$E_{\text{spec}} = \frac{P_{RF}}{F_{CO2}} = \alpha \cdot E_{CO}$$

Conversion efficiency ($\alpha$)

Energy efficiency ($\eta$)

$$\eta = \alpha \cdot \frac{H}{E_{\text{spec}}} = C \cdot \frac{F_{CO2}}{P_{RF}}$$
CO₂ plasmolysis: Experimental insights

Top view

Side view

This project has received funding from the European Union’s Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

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CO₂ plasmolysis: Experimental insights

- Strong pressure dependence
- Low → High confinement modes


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CO₂ plasmolysis: Experimental insights

- Strong pressure dependence
- Low $\rightarrow$ High confinement modes
Mode transition reflected
- in ionisation degree

Ionisation degree

- $P < P_1$
- $P_1 < P < P_2$
- $P_2 < P < P_3$
- $P > P_3$

ionisation degree

- L mode
- H mode

Present work (168 GHz)
 Golubev et al. (176 GHz)
 Derived from plasma width

absorbed power (W)

pressure (mbar)

Perspective: Top view
- waveguide short
- gas nozzle
- microwave
- quartz tube
- field applicator
- exhaust (vacuum pump)
- view-port

Perspective: Side view
- waveguide short
- gas nozzle
- microwave
- quartz tube
- field applicator
- exhaust (vacuum pump)


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CO₂ plasmolysis: Experimental insights

Mode transition reflected:
- in ionisation degree
- in gas temperature (up to 6000 K)

Gas temperature

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CO₂ plasmolysis: Flow pattern

- Strong pressure dependence
- Complex flow pattern

CO₂/CO/O₂
CO₂ plasmolysis: Reactor Model

- Strong pressure dependence
- Complex flow pattern


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**CO₂ plasmolysis: Reactor Model Results**

- Mode transition reflected:
  - in conversion efficiency \( \alpha \)
  - in energy efficiency \( \eta \)

Experiment

Model

- Conversion Eff.


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CO₂ plasmolysis: Reactor Model Results

- Mode transition reflected:
  - in conversion efficiency $\alpha$
  - in energy efficiency $\eta$

Energy Efficiency

- Experiment
- Model

Conversion Eff.

- Experiment
- Model
CO₂ plasmolysis: Reactor Model Results

- Mode transition reflected:
  - in conversion efficiency $\alpha$
  - in energy efficiency $\eta$

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L-Mode (homogeneous): production limited, «low» gas temperatures, low ionisation degree
H-Mode (constricted): «high» gas temperatures and ionisation degrees


At «intermediate» temperatures (~ 3000 K) atomic oxygen production inhibited

At «low» temperatures (1000-2000 K) dominant CO recombination with re-heating of gas

→ Downstream active plasma-zone: efficient gas cooling and product dilution is desired
CO₂ plasmolysis: Design criteria

(Scientific) Design Criteria
... to maximise $\alpha$ & $\eta$ (= indicated area)
CO₂ plasmolysis: Design criteria

(Scientific) Design Criteria & Consequences
... to maximise $\alpha$ & $\eta$ (= indicated area)

i. «low(er)» pressure regime: ~ 150 mbar

ii. efficient gas cooling downstream

iii. $\rightarrow$ Diluted gas stream
CO₂ plasmolysis: Design criteria

(Scientific) Design Criteria & Consequences

... to maximise α & η (= indicated area)

i. «low(er)» pressure regime: ~ 150 mbar
   i. Vacuum pump (compression) required
   ii. Gas mixture (CO/O) is explosive → dilution needed
   iii. Dependence on (sharp) mode transitions
   iv. → Control challenge

ii. Efficient gas cooling downstream
   i. Achievable with
      i. High flow rates (and/or expansion)
      ii. High surface areas
   ii. → High flow rates reduce conversion efficiency α
   iii. → Material challenge: need to withstand >> 1000 K

iii. → Diluted gas stream
   i. (re-)circulation of «inert» gas and bigger size of all components

η = α · \( \frac{H}{E_{\text{spec}}} \) = C · \( \frac{F_{\text{CO2}}}{P_{\text{RF}}} \)
CO₂ plasmolysis: KEROGREEN implementation

(Scientific) Design Criteria & Consequences

i. «low(er)» pressure regime: ~ 150 mbar
   i. Vacuum pump (compression) required
   ii. → Gas mixture (CO/O) is explosive → dilution needed
   iii. Dependence on (sharp) mode transitions
   iv. → Control challenge («flattened» by higher flow rates)

ii. Efficient gas cooling downstream
   i. Achievable with
      i. High flow rates (expansion)
      ii. High surface areas
      ii. → High flow rates reduce conversion efficiency $\alpha$
      iii. → Material challenge: need to withstand >> 1000 K

iii. → Diluted gas stream
   i. (re-)circulation of «inert» gas and bigger size of all components
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CO₂ plasmolysis: KEROGREEN implementation

<table>
<thead>
<tr>
<th></th>
<th>Power [kW]</th>
<th>Frequency [MHz]</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1</td>
<td>6</td>
<td>915</td>
<td>Lab</td>
</tr>
<tr>
<td>(InitSF)</td>
<td>1-2</td>
<td>2450</td>
<td>Lab</td>
</tr>
</tbody>
</table>

Plasmolysis reactor development

Modelling

Phase 1
1 kW, 2.450 \( \rightarrow \) 915 MHz

Phase 2
6 kW, 915 MHz

CO₂ plasmolysis: KEROGREEN implementation

Power

Frequency

Scale

<table>
<thead>
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<th>Phase</th>
<th>Power [kW]</th>
<th>Frequency [MHz]</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1</td>
<td>6</td>
<td>915</td>
<td>Lab</td>
</tr>
<tr>
<td>Phase 2</td>
<td>6</td>
<td>915</td>
<td>Container/Module</td>
</tr>
</tbody>
</table>

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CO₂ plasmolysis: KEROGREEN implementation
CO₂ plasmolysis: Reactor Model & Practise

Potential window of operation

Preliminary results from commissioning under CO₂ plasma conditions

- Experimental data are close to calculations within 10%
- 9 – 10 Nl/min CO output has been shown

Heat map = calculations for final applicator/reactor configuration with special thanks to F. Peeters, based on Wolf et al. J. Phys. Chem. C 2020, 124, 16806−16819
Preliminary results from commissioning under CO\textsubscript{2} plasma conditions

- Experimental data are close to calculations within 10%
- 9 – 10 Nl/min CO output has been shown
- Stability of operation > 1 hour
- “Operator”-free
Downstream Challenges: Dilution & Separation

CO₂

CO₂/CO/O₂

CO₂/CO/O₂

CO₂/CO(O₂)

CO 15-20%
O₂ 7.5-10%

CO < 14%
O₂ < 7%

CO < 14%
O₂ << 0.5 %

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SOEC as oxygen separator: Concept

**O₂ separation**
- Difficult process
- Lack of literature
- SOEC: Electrochemical O₂ pumping

**Plasma electrode reactions**
- O₂ + 4e⁻ → 2O²⁻ (desired)
- CO₂ + 2e⁻ → CO + O²⁻ (neutral)
- 2CO + O₂ → 2CO₂ (unwanted)
SOEC as oxygen separator: Complex requisites

Functionalities

- **Plasma electrode**
  Unconventional mixture \((CO_2/CO/O_2)\)
  Poor CO activity

- **Electrolyte**
  Oxygen ion conductivity
  Low resistance \(\rightarrow\) thin

- **For both electrodes:**
  Mixed electronic & ionic conductivity
  Low overpotential losses (gas composition, \(T\))

- **Overall**
  High oxygen fluxes \((increased\ T)\)
  Stability
  Reduced CO recombination \((reduced\ T)\)

### Plasma electrode reactions

- \(O_2 + 4e^- \rightarrow 2O^{2-}\) (desired)
- \(CO_2 + 2e^- \rightarrow CO + O^{2-}\) (neutral)
- \(2CO + O_2 \rightarrow 2CO_2\) (unwanted)
SOEC as oxygen separator: Steps

<table>
<thead>
<tr>
<th>Size [cm²]</th>
<th>0</th>
<th>0.2</th>
<th>~500</th>
<th>~5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRL</td>
<td>0</td>
<td>1</td>
<td>2-3</td>
<td>3-4</td>
</tr>
</tbody>
</table>

- **Literature review and material synthesis**
- **Catalytic tests**
- **Electro-catalytic SOEC tests**

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Key findings

- **OCV conditions**
  - As the operation T is increased CO losses (via CO oxidation) are also increased

- **Under polarization**
  - Oxygen removal is favoured at high T due to higher current densities.
  - Increasing the applied potential is a knob to increase the amount of CO via CO₂ electrolysis.
  - Faradaic efficiency is high (> 90%)
Downstream Challenges: Separation by SOEC

CO₂ → CO₂/CO/O₂ → CO₂/CO/O₂ → CO₂/CO/(O₂)

1. Plasmolysis reactor
2. Microwave resonator
3. Solid oxide electrolyte cell

A Pandiyan et al, Journal of CO₂ Utilization 57 (2022) 101904

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Downstream Challenges: Separation by SOEC

- Several testbenches for performance test of cell-stacks
- Implementation (integration) with plasmolysis gas stream
- Performance of individual cells not reproduced

**Diagram: CO₂ → CO₂/CO/O₂ → CO₂/CO/O₂ → CO₂/CO/(O₂)**

1. Modified (comm.) stack
2. Testbench for stack

**Phase 2**

6 kW / 915 MHz

**O₂**

**CO₂/CO/O₂**

**CO₂/CO/O₂**

**CO₂/CO/(O₂)**

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Summary / Take home messages

- **KEROGREEN** project
  - CO₂ & electricity ➔ Kerosene
  - Public event 27/09/2022

- **Plasmolysis of CO₂**
  - Conversion process dominated by strong and sharp gradients
  - Scientifically desired conditions form challenges for technical implementation
  - Standalone, operator-free, “plug-&-play” gas conversion module realised
  - Heat integration not (yet) considered

- **Oxygen separation**
  - SOEC approach promising on cell level
  - Testbenches realised for different scales
  - Upscaling and process integration seems to need radically new stack design
Any Questions?