DIFFER KIT Karlsruhe Institute of Technology vito Cerpotech HYGEAR INERATEC

Production of Sustainable aircraft grade Kerosene from water and air powered by Renewable Electricity, through the splitting of CO_2, syngas formation and Fischer-Tropsch synthesis

KEROGREEN FINAL EVENT

27.09.2022 @ KIT-IMVT

CO_2 Neutral Fuels by Adelbert Goede

Project Coordinator

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

The Energy Transition

Renewable Electricity Share in EU reaches 37% in 2020

➢ Well underway to reach EU 2030 Target of 40% renewable energy!

Or is it ??

- Electricity only 20% of energy mix > Mobility, High temperature Industrial heat Low temperature domestic heat, Agriculture/waste disposal/mining **not covered**

Requires:

- Doubling deployment rate of solar and wind capacity this decade
- Coping with intermittency and seasonal mismatch of supply and demand

Problem already:

- Grid congestion, dynamic response > curtailment > wasting renewables

This project has received funding from the European Union's Horizon 2020 Research and Innovation

Power to X : The way to go

What is Needed?
Long-duration (seasonal, interannual) and large scale (PJ) electricity storage

Solution:
Energy storage in high energy density fuels and chemicals
- converting air (containing CO_2, N_2 species) and water into high energy density products, powered by (surplus) electricity

Power to X (PtX) is key technology (X = Liquid Fuel)
Couples the power sector to chemical, heating and fuel sectors

Mobility is case in point, depends heavily on energy dense fuels
➢ Aviation is the extreme case considered here

This project has received funding from the European Union's Horizon 2020 Research and Innovation

Options for Sustainable Aviation Fuel

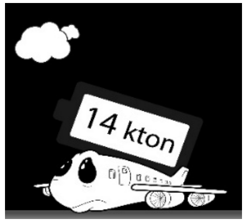
DIFFER

Hydrogen: low energy density (1/3000 kerosene) – **too bulky**

- liquefied at **20K: energy density factor 4.5 lower** than kerosene,
- pressurised at **700 bar**: energy density **factor 6.7 lower** than kerosene

➢ New aircraft design, fuel system, ground handling and storage system

Short haul flight perhaps -> Qualification will take > 10 yrs and > 100 M$



Batteries: low specific energy (1/50), low energy density (1/14)

- Long haul aviation not feasible – **too heavy**

Airbus A 380 needs 14.000 ton battery to replace its 260 ton kerosene pay-load

Hybrid: DLR H_2 Antares 1-seater, range 750 km, speed 170 km/hr, alt 4 km

36 kW PEM Fuel Cell @ 80 kg, 10 kWh battery 45-60kW @ 50kg

Why not take the train instead?

Bio Fuel: Current EU policy

- Food vs. Fuel vs. Flora trilemma – **there is not enough of it**

current kerosene consumption ~ 5 Mbarrel/day > requires 2 to 5 x NL area to grow

The third way: CO_2 Neutral Kerosene

DIFFER

Why CO_2 neutral kerosene?

- Climate Neutral fuel for long haul transportation
- Existing engine technology and infrastructure
- Long term (seasonal), large scale (EJ) Energy storage and Energy security
- Air Pollution reduction: No Sulphur, No soot, Lower NO_x

What are the Challenges?

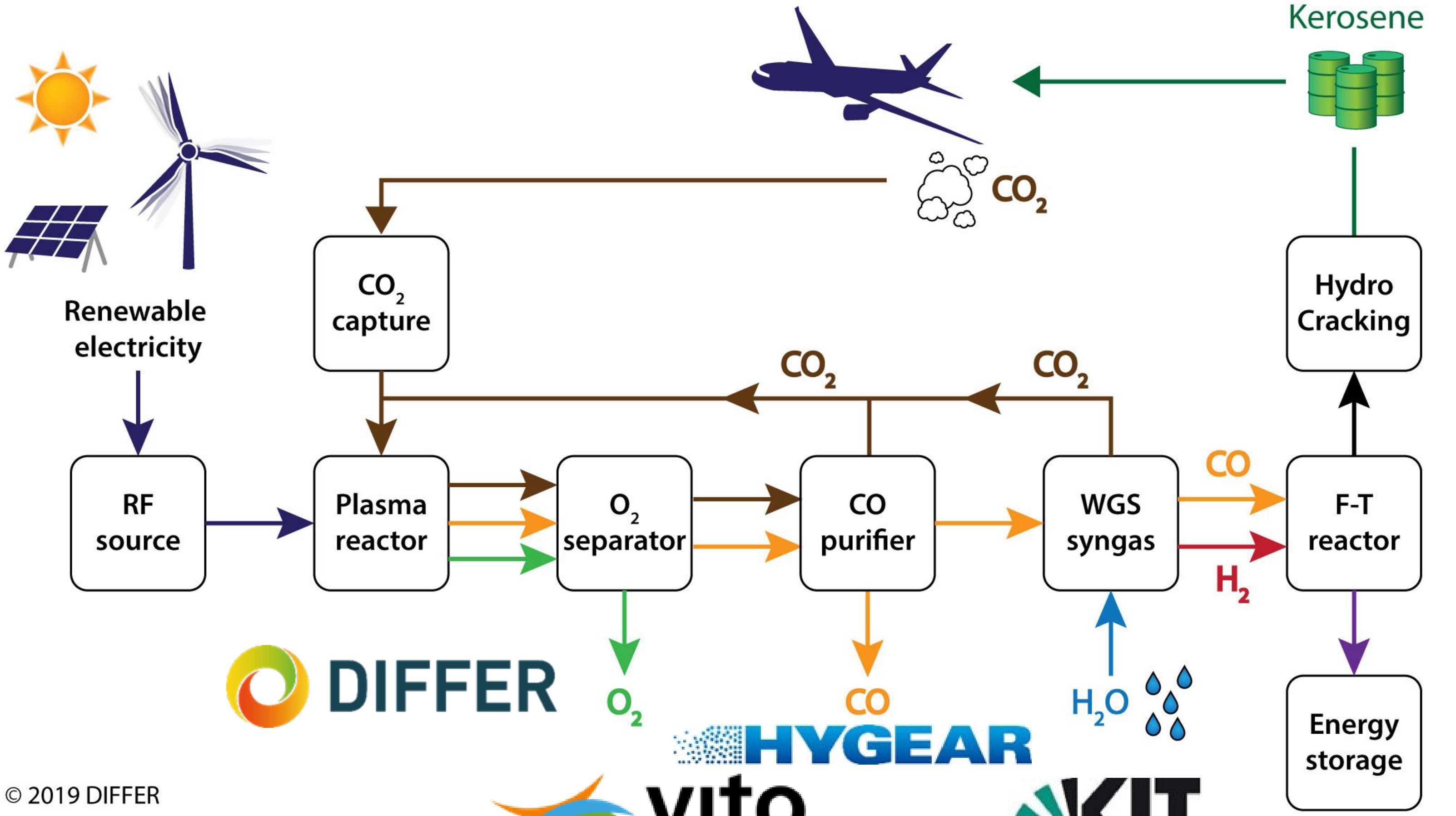
- Conversion of air N_2, H_2O, CO_2 into energy dense fuels by PtX technology
- System Integration: compact, decentralised, dynamic operation
- Direct Air Capture of CO_2 to render the fuel cycle CO_2 neutral

From proposal to EU Horizon 2020 funded project:

- EU H2020 LCE call > 1st stage 2016 > 2nd stage 2017 > Selected end 2017
  KEROGREEN project start 1 April 2018 > Project ends 30 Sept 2022

This project has received funding from the European Union's Horizon 2020 Research and Innovation

KEROGREEN Concept and Consortium



- CO_2 gas captured from ambient air is split by the plasma reactor into products CO_2, CO, O_2
- The O_2 is separated out electro-chemically
- The CO content purified
- CO and water forms syngas
- Fischer-Tropsch reactor synthesizes hydrocarbons
- Hydrocracking to optimize kerosene content
- Upon combustion: CO_2 re-emitted into the atmosphere
- Direct Air Capture (not part of project) closes the Circle

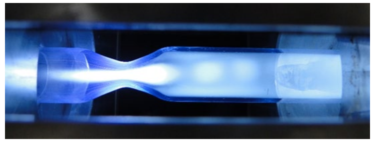
This project has received funding from the European Union's Horizon 2020 Research and Innovation

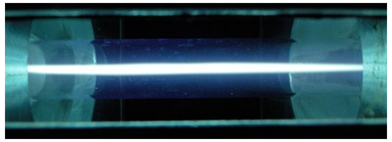
CO_2 conversion by Plasmolysis

DIFFER

2012: First DIFFER experiments on CO_2 plasma splitting
4 measurement campaigns in collaboration with Univ of Stuttgart - IGVP
Inspired by Russian research in the 1960-70's, see Rusanov, Legasov et.al
First DIFFER publication:

[1] A.P.H. Goede, et. al., EPJ Web of Conferences **79**, 01005 (2014), DOI*: 10.1051/epjconf/20147901005*





Objective:

CO_2 splitting by channelling energy into molecular vibrations to break the strong chemical bond, not to heat the gas (non-equilibrium chemistry $T_{vib} > T_{gas}$)

- High productivity: large gas flow (75slm), power density (45W/cm^2)
- Fast dynamic response to intermittent power supply
- No scarce materials employed
- Favourable upscaling (volume vs. surface process)

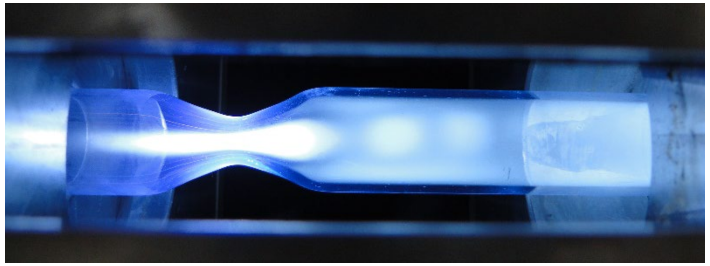
This project has received funding from the European Union's Horizon 2020 Research and Innovation

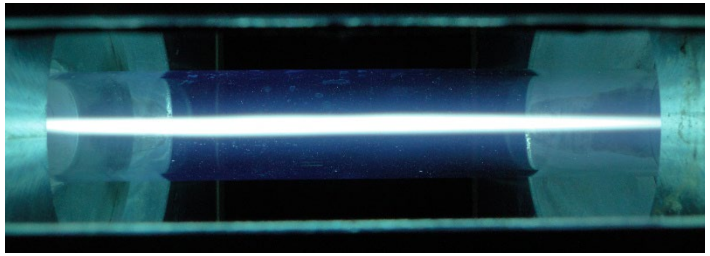
First measurement results

Two modes of operation identified depending on gas pressure:

1. Low density dilute plasma, low ionization degree
2. High density filamentary plasma, high ionization degree

Mode switch around 100mbar





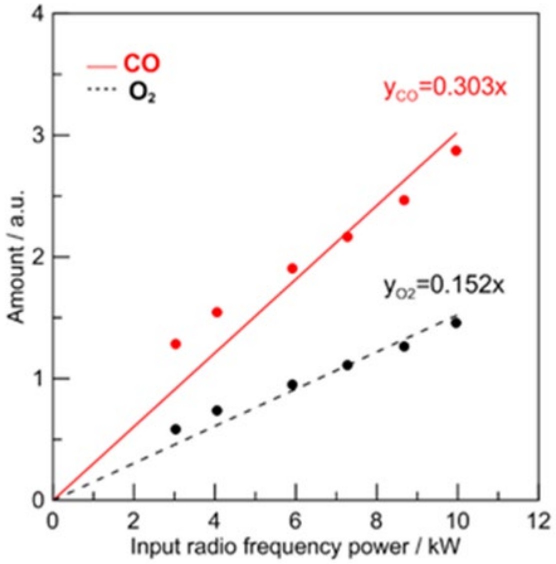
CO production increases **linear** with **power**

O_2 increase in stoichiometric ratio

$\eta = H/E_{CO}$ energy efficiency

$\alpha = E_v/E_{CO}$ conversion

$\eta = CF/P_{RF} = \alpha\, H/E_v$ [1]



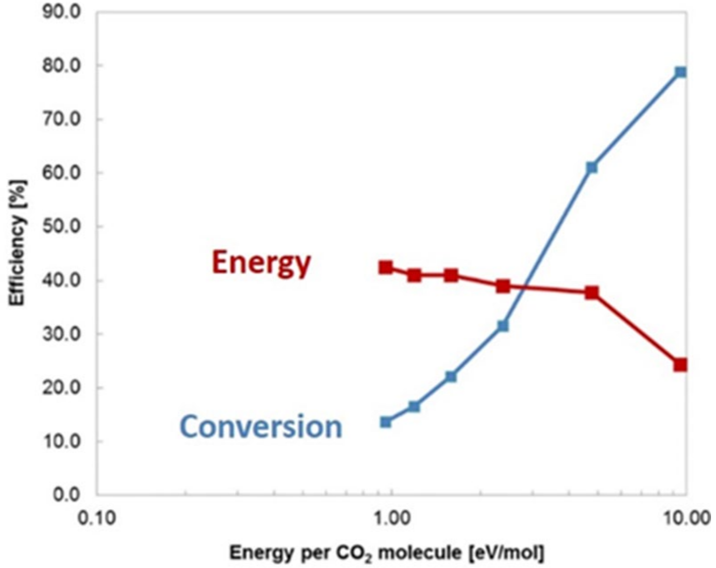
Energy efficiency η and **CO conversion yield α**

- Communicating vessels
- No economic advantage

H = Minimum Enthalpy

E_{CO} = Energy to form CO

E_v = Energy per incoming CO_2

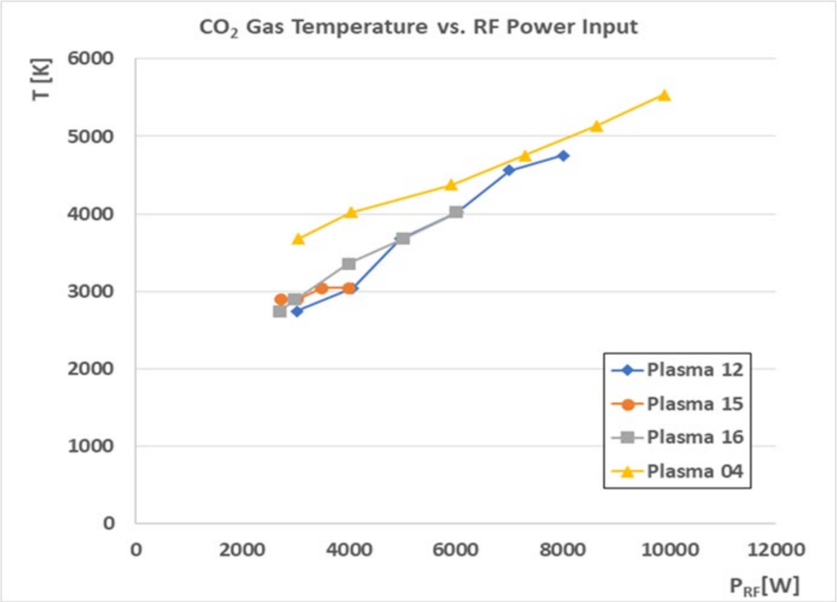


Early Russian work

Russian claim of the seventies: 90% energy efficiency
Low energy (<1eV) plasma electrons excite vibrations in CO_2 molecule
Vibrations drive chemistry by vibrational ladder climbing to dissociation limit
Vib -Tran relaxation is kept low by T<1000K

Chemical reaction scheme

CO_2 → CO + O (ΔH=5.5 eV)
followed by reuse energetic **O** radical
CO_2 + O → CO+ O_2 (ΔH=0.3 eV)
Net
CO_2 → CO + ½ O_2 (ΔH=2.9 eV)



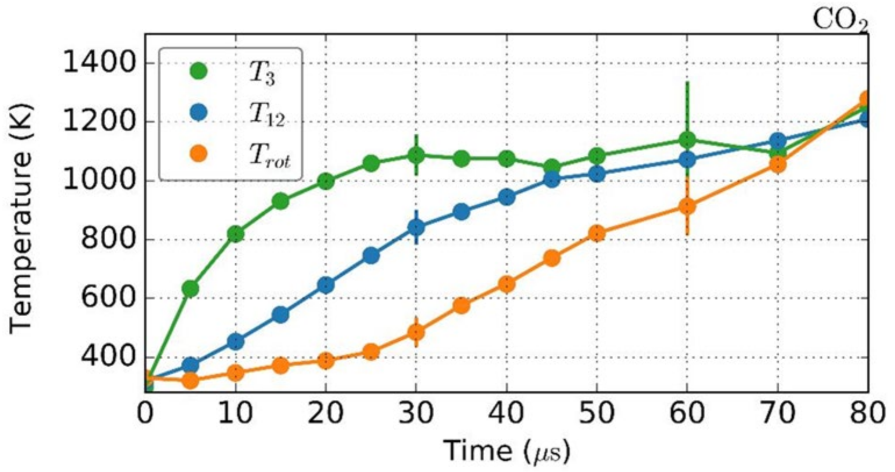
Requirements:

- Thermal non-equilibrium, gas temperature < 1000 K
- Follow-up reaction with atomic oxygen to occur
- CO product extractable from plasma discharge

Measurement:

CO_2 gas temperature increases with input RF power to over 5000K.
Non-equilibrium condition not met

New Insights: Vibrational vs. thermal dissociation

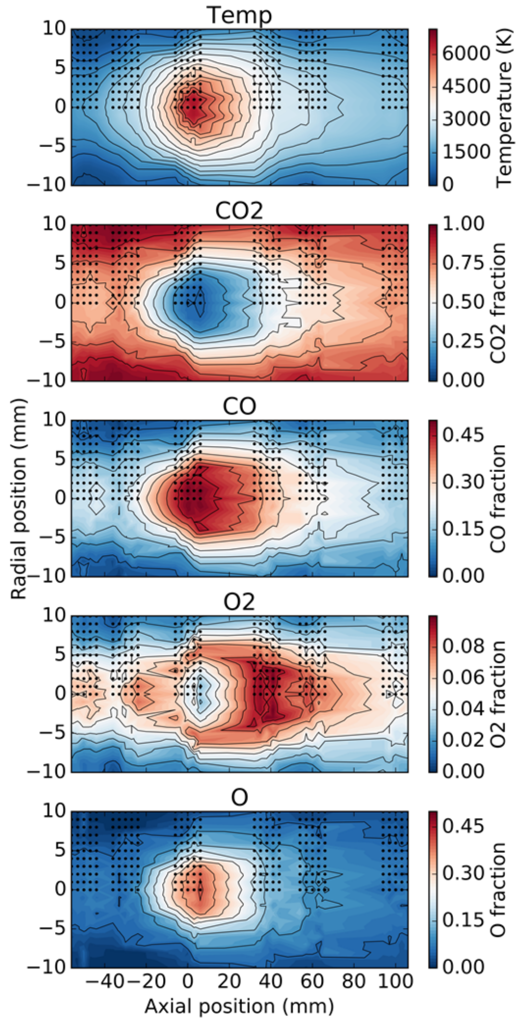


T_3 asymmetric stretch mode
T_{12} bending mode
T_{rot} proxy for T_{gas}

Raman spectroscopy reveals:

<- **Time dependence** of CO_2 heating

2D resolved distributions of -> temperature and concentration CO_2, CO, O_2 and O



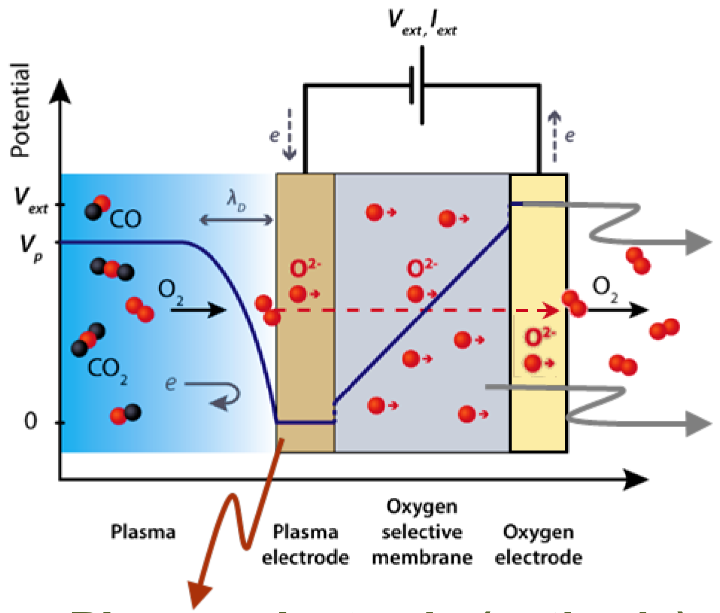
Results

1. Thermalisation sets in after 30 µs
Non-thermal equilibrium only during plasma ignition phase

2. CO and O formation in hot core
Thermal dissociation condition

Ref. **Alex van de Steeg** et.al. ACS Energy Lett. 2021, 6, pp 2876-2881
Alex van de Steeg et.al. Plasma Sources Sci. Technol. 2020,29, 115001

Oxygen separation – Material selection



High temperature solid oxide electrochemical cell for separation O_2 from the CO_2, CO, O_2 gas mixture

Oxygen electrode (anode): LaSrCoFe with GaDCe interlayer, porous for good oxygen conductivity, serving as mechanical support

Electrolyte: thin YSZr for sufficient O^{2-} conduction, yet withstanding voltage gap

Plasma electrode (cathode)

- Electronic conductivity (e^-)
- Ionic conductivity(O^{2-})
- Low catalytic activity to CO
- Electro-chemical stability
- Mechanical stability

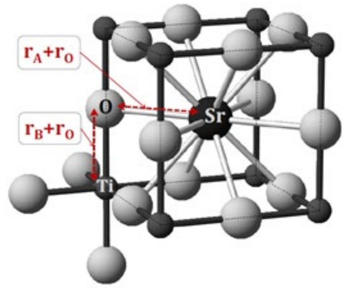
→ **Perovskites**

$Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM)

Also tried: LaSrZnTi (LSZT)

Powders supplied by Cerpotech

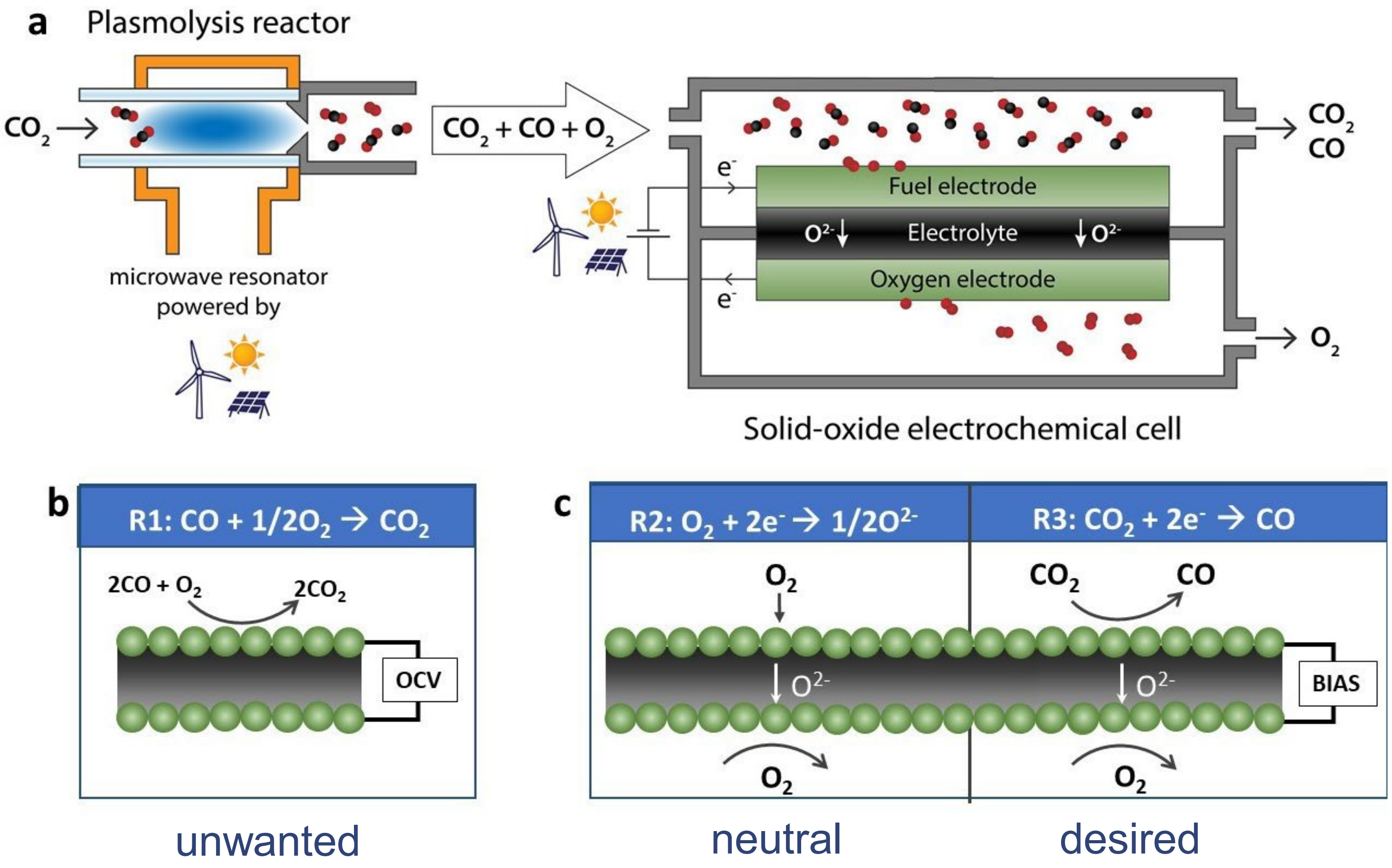
Underlying membrane research by VITO



[1] Adelbert P. H. Goede *CO_2 Neutral Fuels* EPJ Web of Conferences **189**, 00010 (2018)

[2] A. Pandiyan et.al. J. CO2 Util, 57 (2022) 101904 https://doi.org/10.1016/j.jcou.2022.101904

Oxygen separation – Validation



Important 2022 Result

Coupled plasma-electrolysis process yields

- ***91% less O_2*** *and*
- ***138% more CO***

In the exit gas stream compared with plasmolysis alone

No degradation observed in durability test

Ref **A. Pandiyan et.al.**
J. CO_2 Util, 57 (2022) 101904
https://doi.org/10.1016/j.jcou.2022.101904

More details in presentation Stefan Welzel

Kerosene synthesis and System Integration

***CO purifier** by HyGear:* CO yield after purification 78% at 98% purity
(target CO yield for industrial scale was 68 % at 96 % purity)

***Water Gas Shift reactor** at KIT:* Enhanced by CO_2 sorbent and catalyst, Dynamic operation and modelling

***Fischer-Tropsch reactor** at INERATEC:* based on high heat transfer micro-structured reactor, with Co-based catalyst, heat integration at system level

***Hydro-Cracking reactor** at KIT:* hydration of the FT crude, isomerization to alkanes, no aromata, no alkenes

***System Integration** at KIT*

Integration of 6 modules of varying TRL into one consistent system with matched gas flow, pressure and power.

Stepped approach: O_2 separator not yet integrated, upscaled O_2 separator integrated, recirculation CO_2 and heat integration.

LCA on energy and material flows, CAPEX and OPEX preliminary numbers

more details in presentation Peter Pfeifer, followed by *Site visit*

Summary

DIFFER

KEROGREEN offers a **novel route** to sustainable aviation fuel (**SAF**), powered by renewable electricity:

- Departs from **recirculated CO_2** rather than H_2 , employing **plasma technology**
- Meets climate and environmental requirements of UN-ICAO, EU Green Deal and COP-26 Glasgow 2021, UN - CORSIA 2019 and EC-RTD-CETP-Clean Aviation

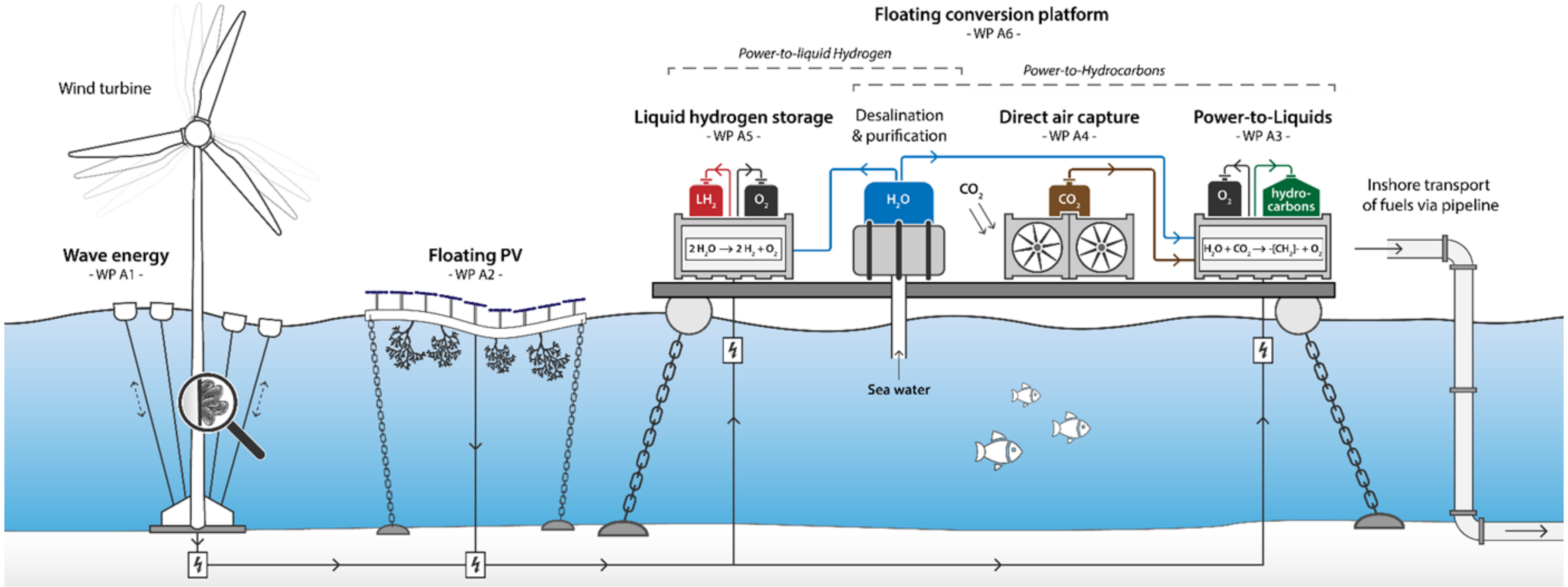
Results:

- CO_2 conversion in CO and O_2 reaches 90%, scales linear with RF plasma power
- Energy efficiency improvement by ongoing plasma reactor development
- Feasibility of oxygen separation from CO gas stream demonstrated
- System Engineering of the integrated process established
- Efficiency improvement through heat integration and recirculation of separated CO_2
- Techno-economic assessment on sustainable kerosene
- Sustainability assessment on energy and material streams

Main Challenges and Future Outlook

- **System Integration** to reach full performance
- **Upscaling**
- **Cost reduction**

Ultimately: decentralised, off-shore, PtX-DAC system, close-coupled and sized to the renewable electricity source (MW)



Acknowledgement

Michalis Tsampas[1], Arunkumar Pandiyan[1], Suleyman Er[1], Ilker Tezsevin[1], Roland Dittmeyer[2], Peter Pfeiffer[2], Francisco de Sales[2], Tabea Stadler[2], Michael Klumpp[2], Andreas Patyk[2], Manuel Andresh[2], Sabine Müller[2], Vesna Middelkoop[3], Marijke Jacobs[3], Anne Dalager-Dyrli [4], Leif Olav Jøsang[4], Sophie Labonnote-Weber[4], Evgeniya Khomyakova[4], Leonardo Roses[5], Ellart de Wit[5], Tim Böltken[6], Friedemann Timm[6], Linus Schulz[6], Alexander Alekseev[7], Maarten van Dijk[8], Richard van de Sanden[1], Waldo Bongers[1], Martijn Graswinckel[1], Ben Elzendoorn[1], Paola Diomede[1], Pedro Viegas[1], Bram de Wolf[1], Floran Peters[1], Alex van de Steeg[1], Erik Langereis[1]

1. DIFFER, Dutch Institute for Fundamental Energy Research (NWO)
2. KIT, Karlsruhe Institute of Technology (Helmholtz Association), Institutes IMVT and ITAS
3. VITO, Vlaamse Instelling voor Technologisch Onderzoek NV
4. Cerpotech, Ceramic Powder Technology AS
5. HyGear B.V
6. INERATEC, Innovative Chemical Reactor Technologies GmbH
7. LINDE AG
8. SkyNRG

I should also like to thank EC - CINEA staff serving as Project Officer/Cluster Manager for the KEROGREEN LCE project
Olja Kristic, Javier Garcia-Fernandez, Maria Moragues-Canovas and Laura Gomez-Lozano

Enquiries:
Adelbert Goede
Dutch Institute for Fundamental Energy Research
De Zaale 20, 5612 AJ EINDHOVEN
a.p.h.goede@differ.nl
www.differ.nl

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

Any Questions ?

DIFFER

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