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

Highlights from KEROGREEN's plasma-route towards e-Kerosene

Stefan Welzel (DIFFER)
Peter Pfeifer (KIT)

Final Event, 27th September 2022

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

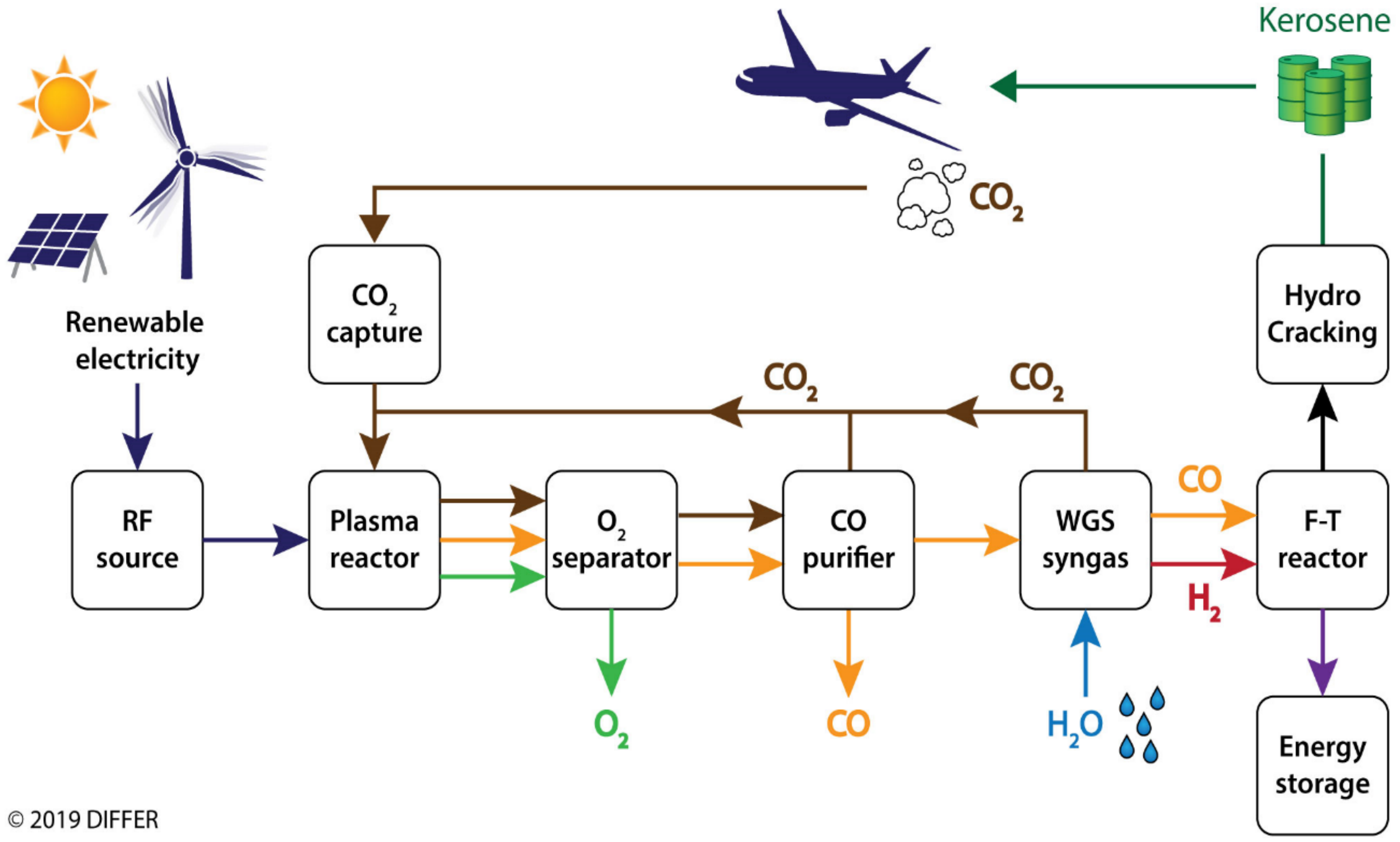
Overview

- Process chain
  - Plasmolysis to split CO_2 into CO and O_2
  - Oxygen separator including material and membrane development
  - CO Purification

  - Syngas generation by sorption-enhanced water gas shift (SE-WGS)
  - Fischer-Tropsch (FT) Synthesis to produce hydrocarbons
  - Hydrocracking (HC) of long hydrocarbon chains to produce Kerosene crude
- Full process integration
- Process efficiency
- Life cycle assessment

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

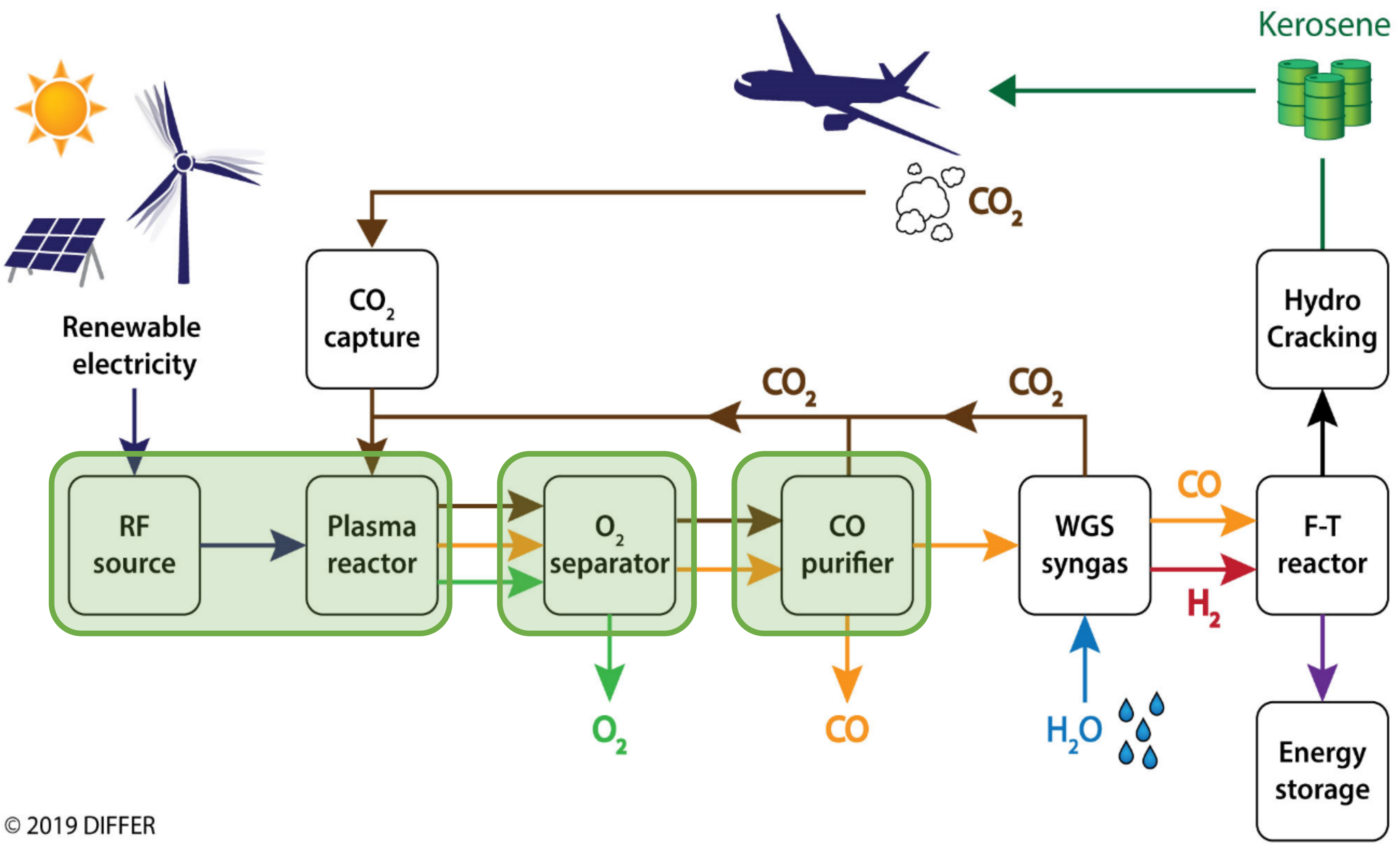
The process



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

Upstream processes

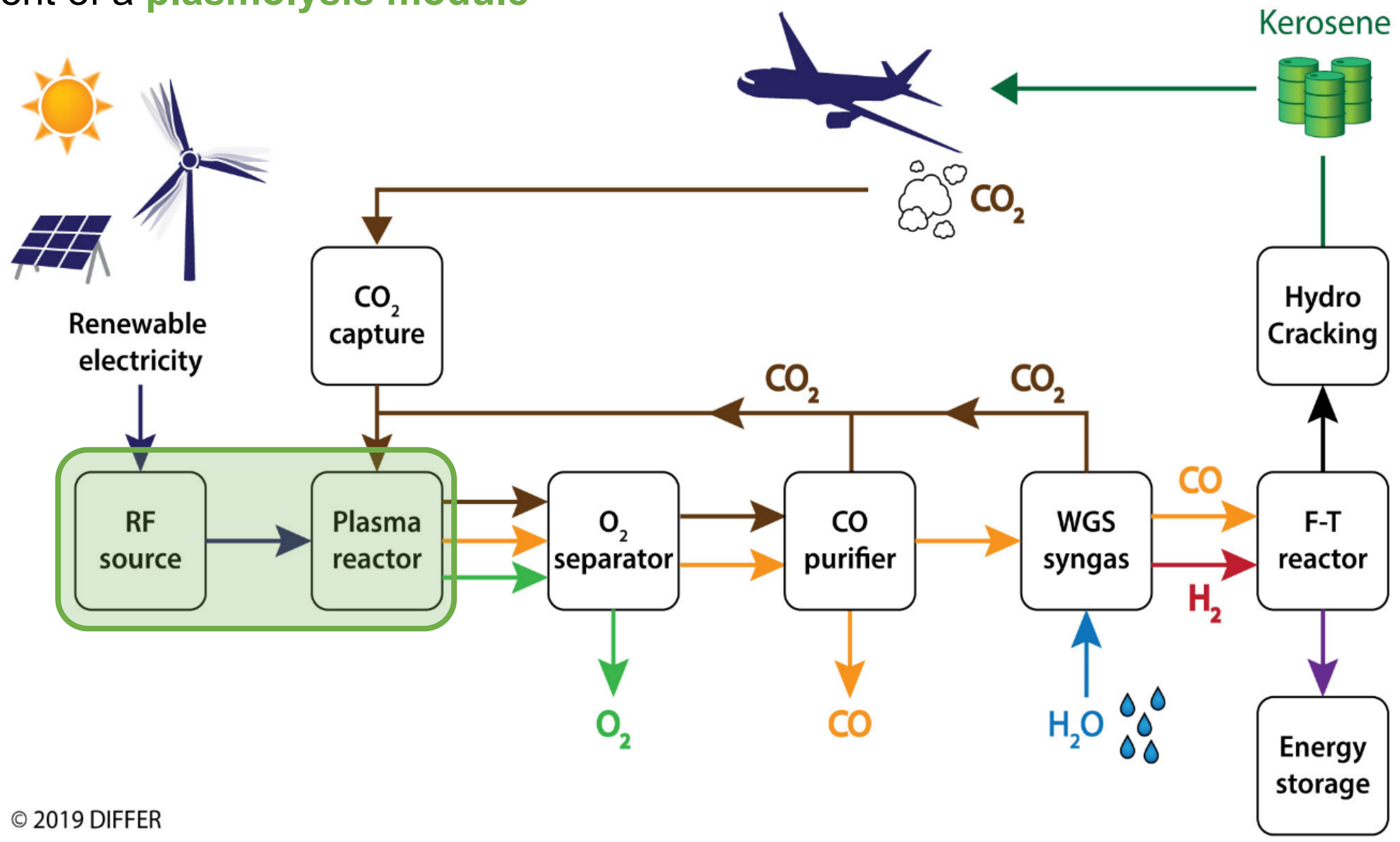
DIFFER



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

Upstream processes

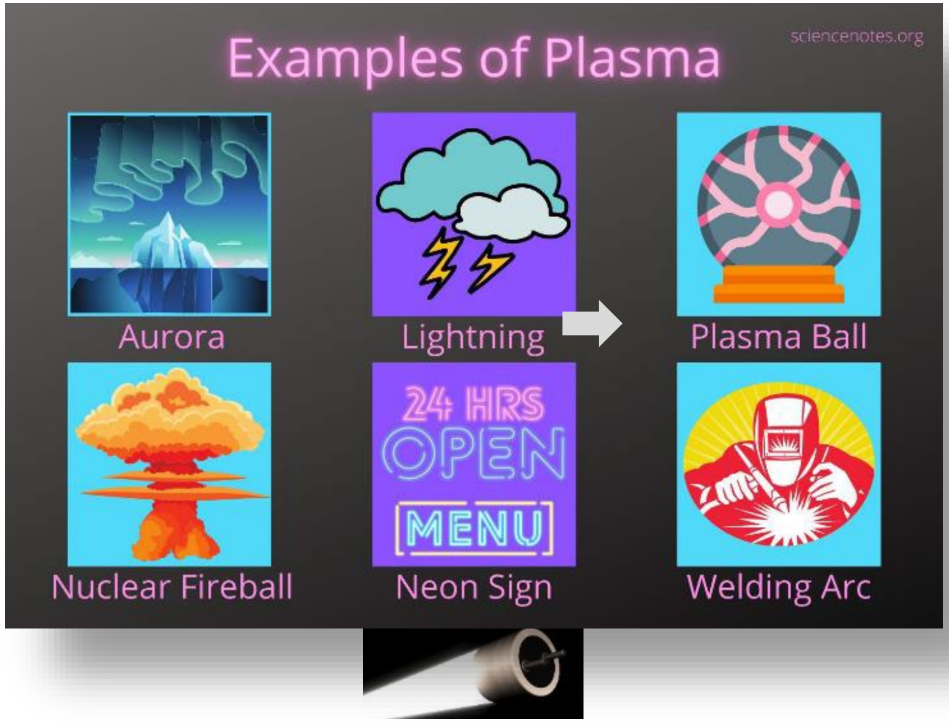
- Development of a **plasmolysis module**



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

Plasmolysis: What is a plasma?

Typical plasmas (= gas discharges)



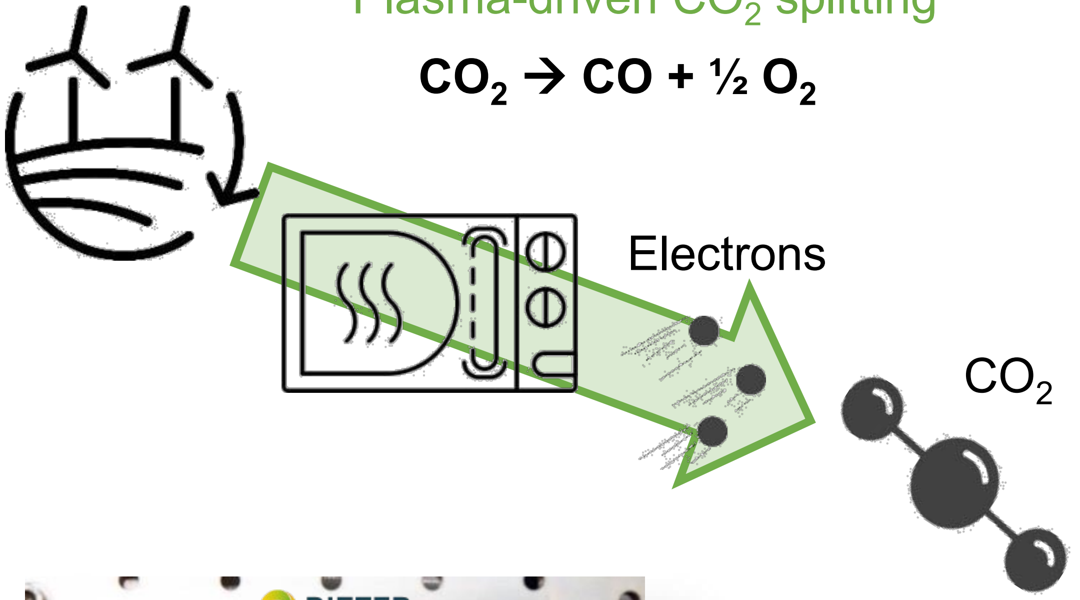
- Driven by electricity (only)
- "Switchable" (= no inherent inertia)

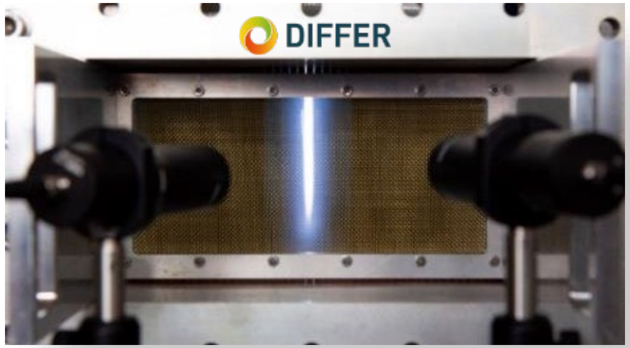
https://sciencenotes.org/20-examples-of-plasma-physics/

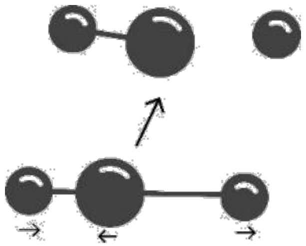
Our approach

Plasma-driven CO_2 splitting

$CO_2 \rightarrow CO + ½ O_2$





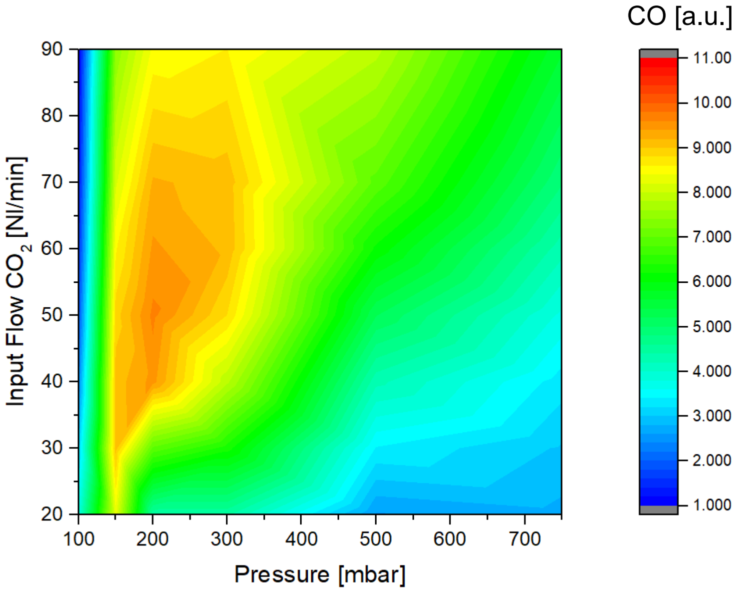


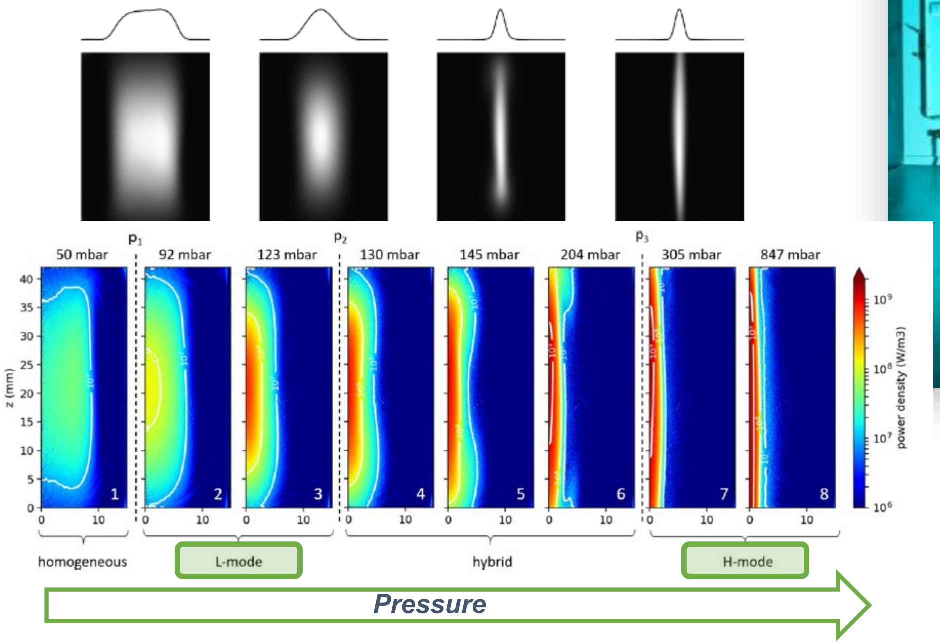
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Plasmolysis Module

DIFFER

- New container-sized module developed from scratch (2450 → 915 MHz)
- “Operator-free”, turn-key module (6 kW_{el})
- **Key figures**
  - Output: 0.7 kg CO / h (15 … 35% conversion)
  - Energy cost: 0.12 kWh/kg CO





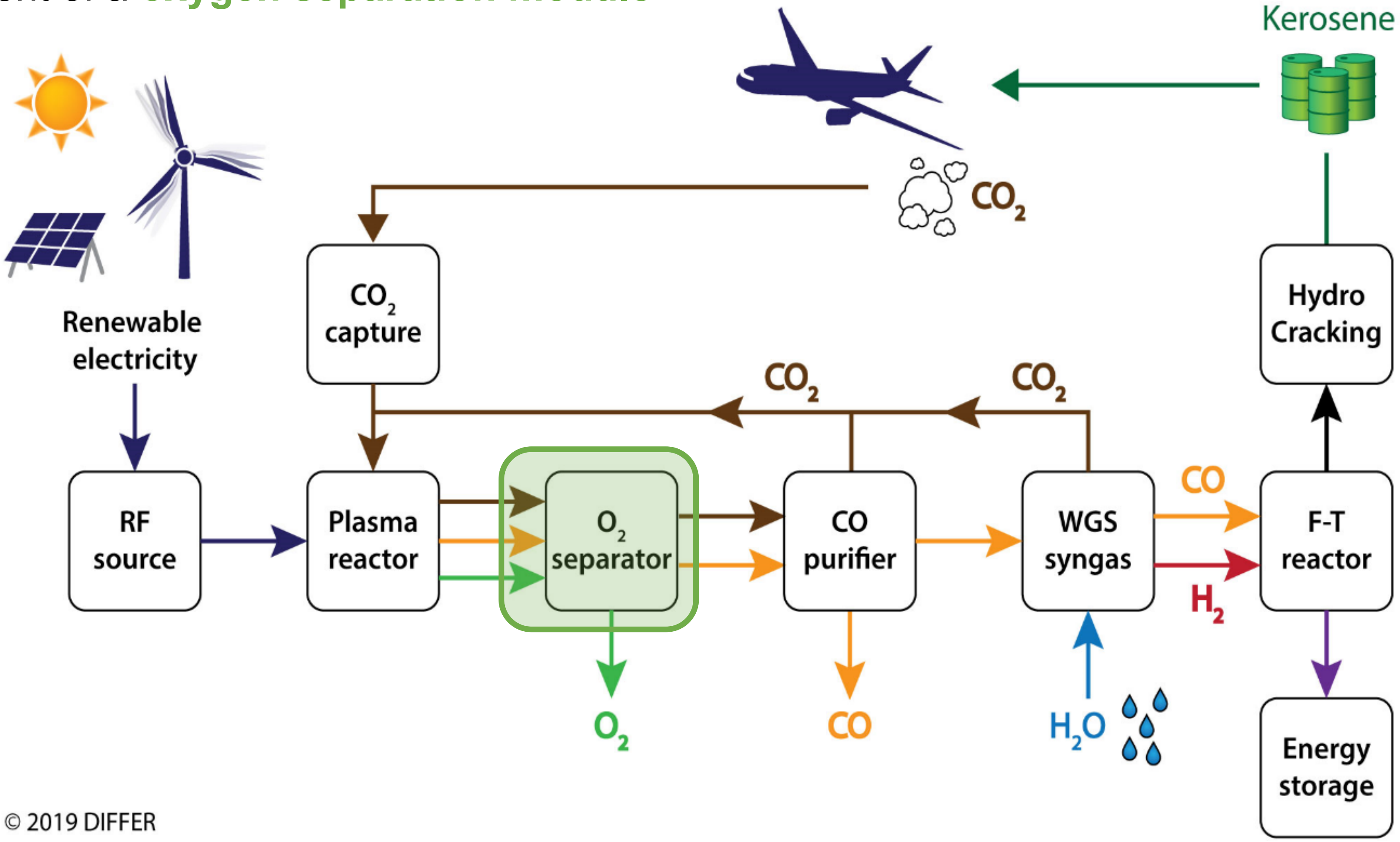
- Non-linear process characterised by strong gradients and (local) temperatures >> 1000 K

AJ Wolf PhD Thesis, Eindhoven Univ. Technology, 2021

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

Upstream processes

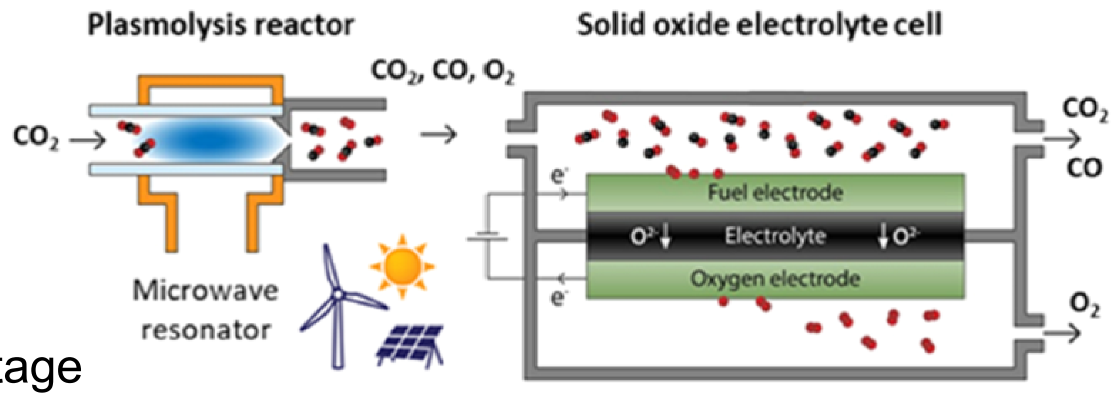
- Development of a **oxygen separation module**

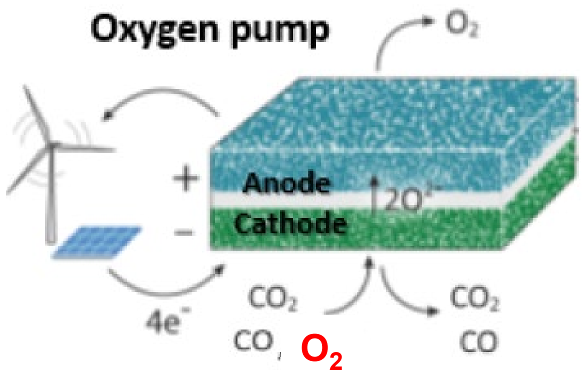


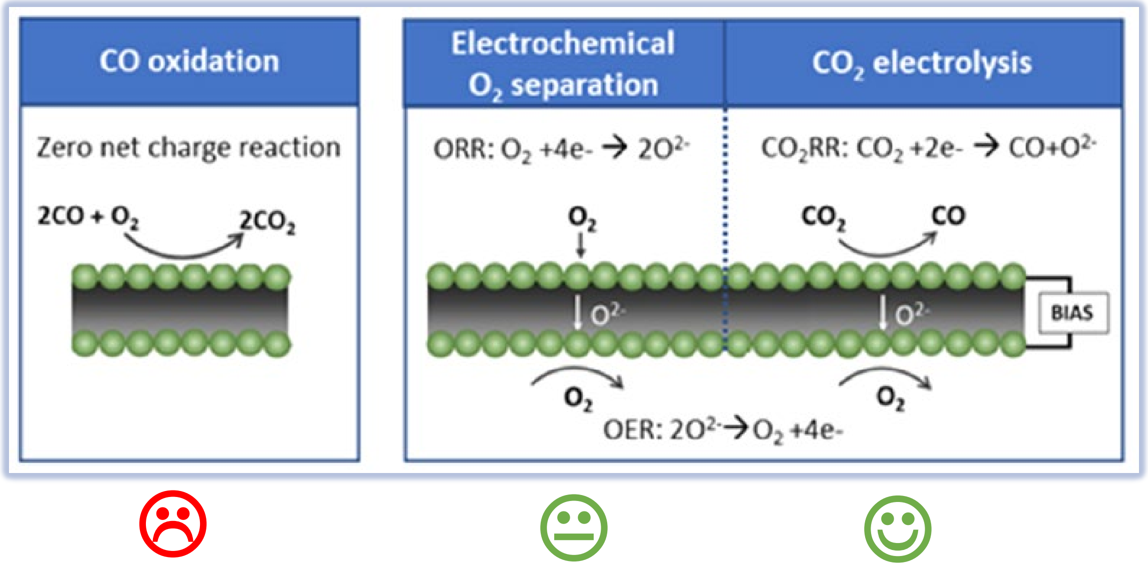
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Oxygen separation: Our electrochemical approach

- Oxygen separation
  - Complex (difficult) process
  - Lack of literature 🡨 🡪 Material challenge
- Electrochemical approach
  - Oxygen (ion) conduction electrolyte
  - **S**olid **O**xide **E**lectrolyte **C**ell (SOEC)
  - Electrochemical oxygen pumping upon applied voltage





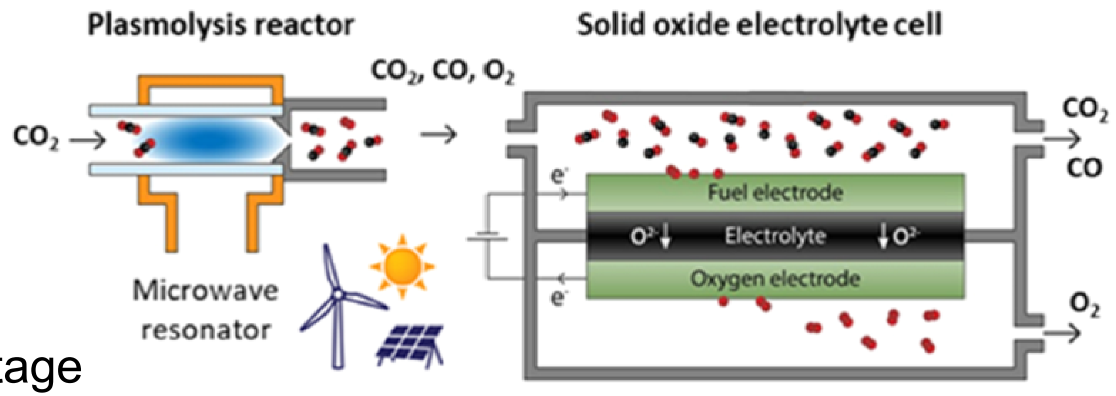


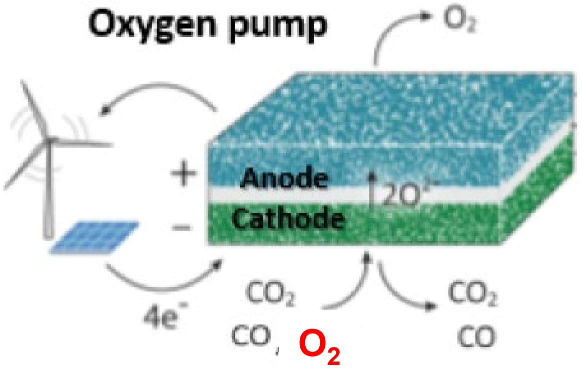
A Pandiyan et al Journal of CO_2 Utilization 57 (2022) 101904

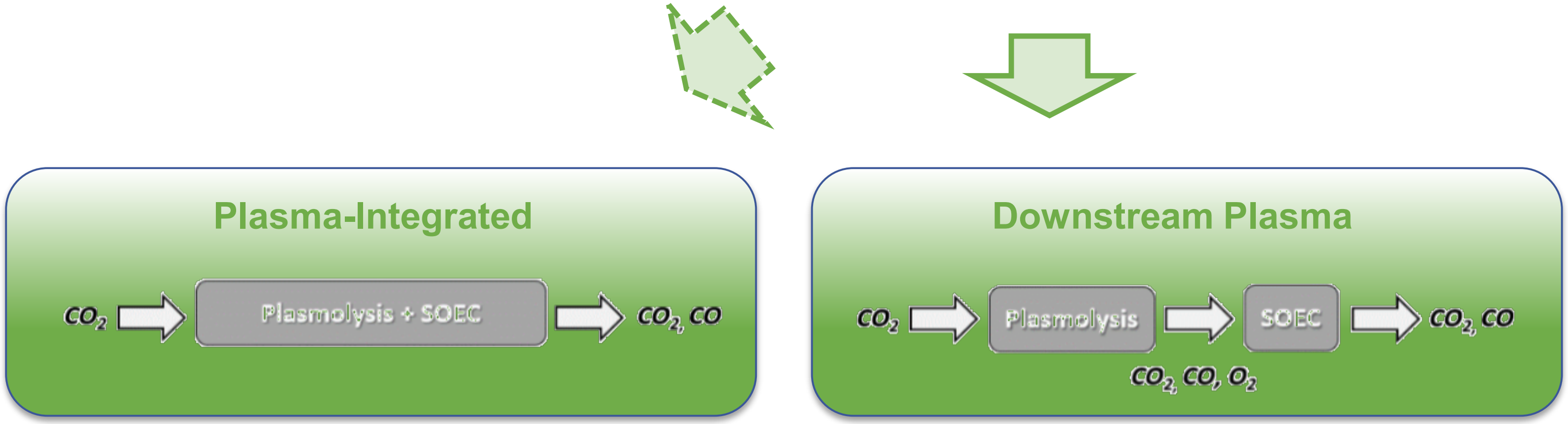
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Oxygen separation: Our electrochemical approach

- Oxygen separation
  - Complex (difficult) process
  - Lack of literature 🡐 🡒 Material challenge
- Electrochemical approach
  - Oxygen (ion) conduction electrolyte
  - **S**olid **O**xide **E**lectrolyte **C**ell (SOEC)
  - Electrochemical oxygen pumping upon applied voltage





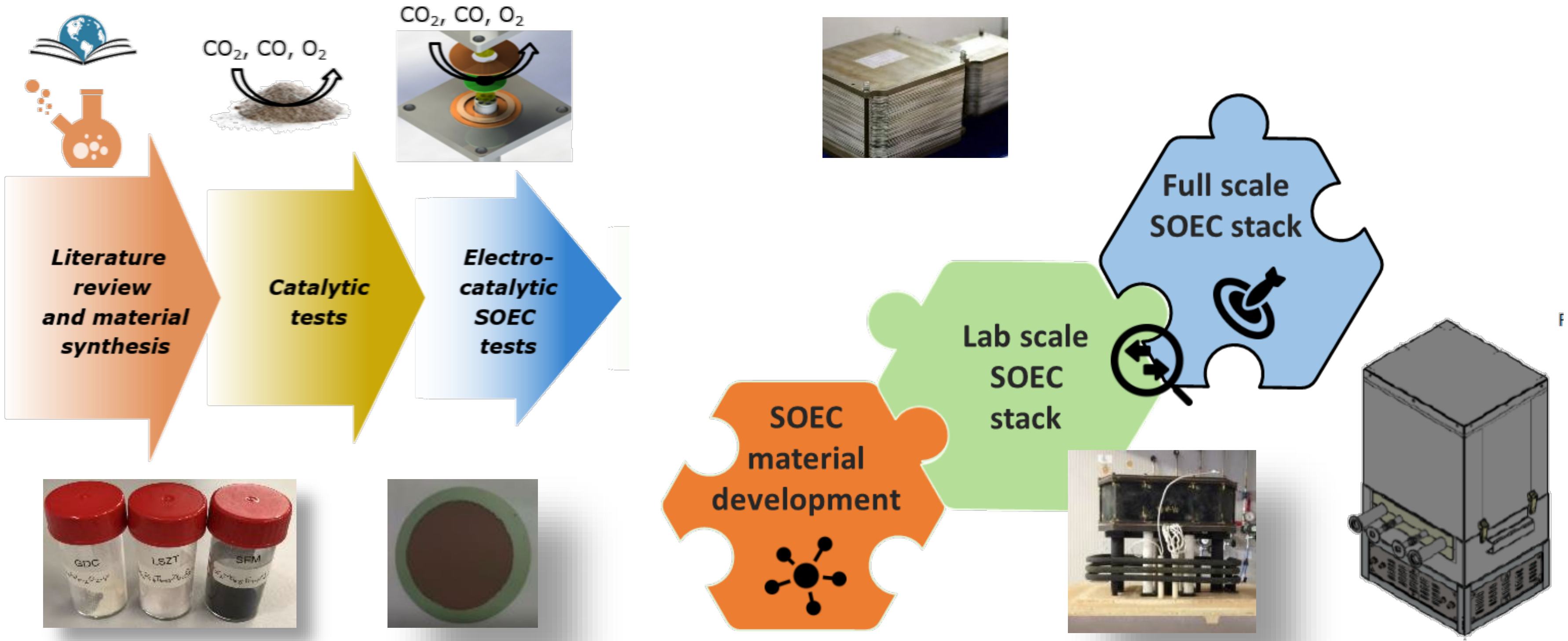


A Pandiyan et al Journal of CO_2 Utilization 57 (2022) 101904

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

Oxygen Separation: Module Development

Steps to be taken: From material design towards cell stack integration



Integrated stack module at full technical scale

©DIFFER/B. v Ovebeeke

Size [cm^2]	0.2	~ 500	~ 5000
Power [kW$_{el}$]	0.0003	0.15	1.5

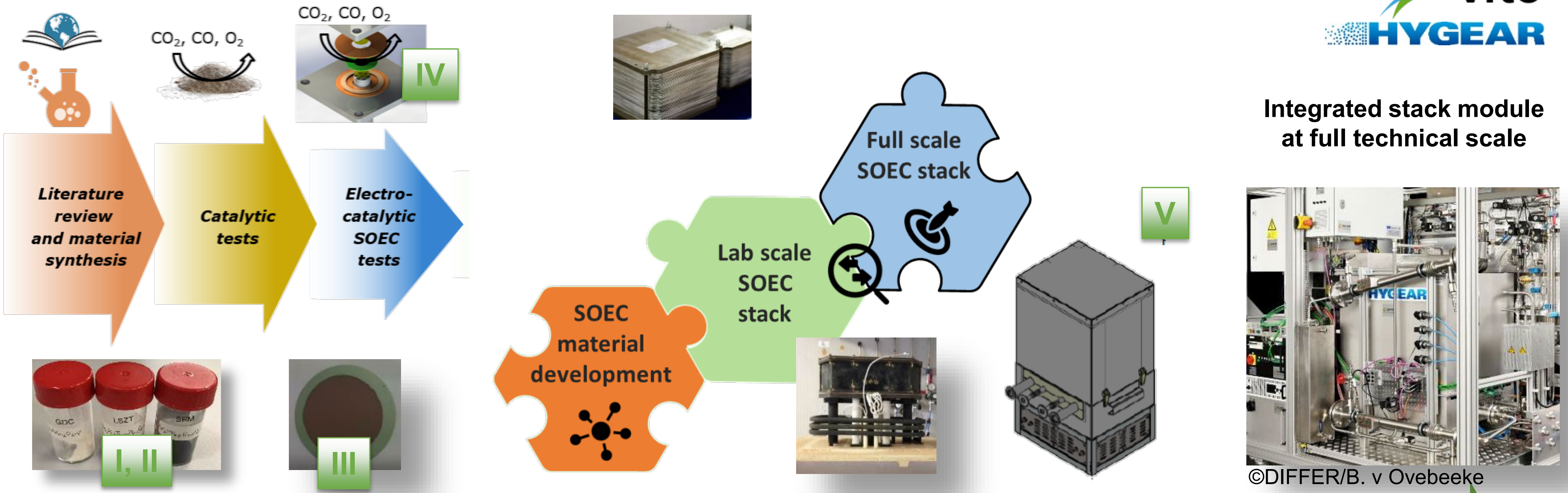
Barelli et al Energies 13 (2020) 6173
www.sofc-fuelcell.com

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

Oxygen Separation: Module Development

DIFFER
Cerpotech
vito
HYGEAR

Steps to be taken: From material design towards cell stack integration



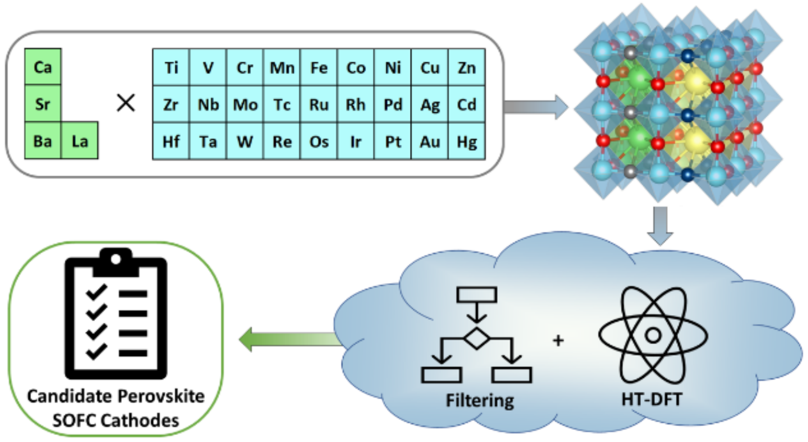
Size [cm^2]	0.2	~ 500	~ 5000
Power [kW_{el}]	0.0003	0.15	1.5

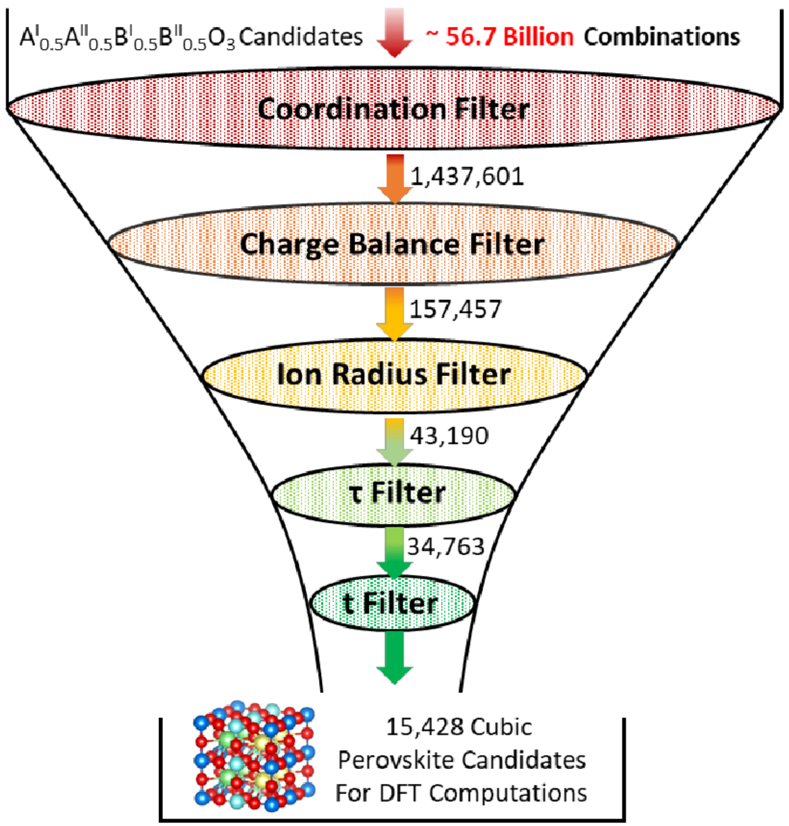
Barelli et al Energies 13 (2020) 6173
www.sofc-fuelcell.com

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

Oxygen Separation I: Material Screening

Automating 3D materials discovery using **High-Troughput – DFT calculations**





Computer simulations

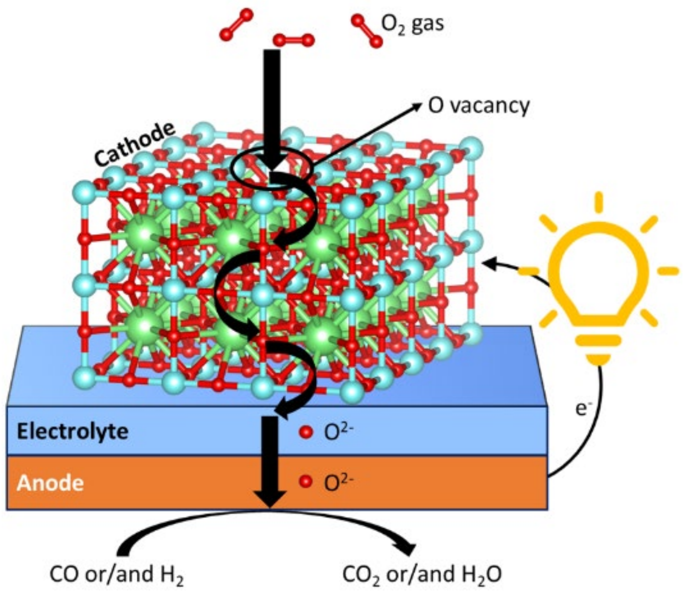
→ **Predict** properties

→ **Suggest** new materials

→ **Easy** to reproduce

Which perovskites are good for

- CO_2 catalysis?
- O_2 catalysis?
- O transport?
- H_2 production?
- … etc. ?

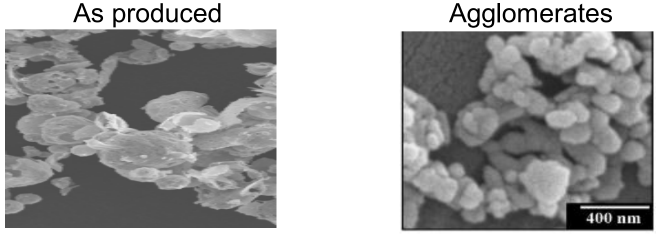


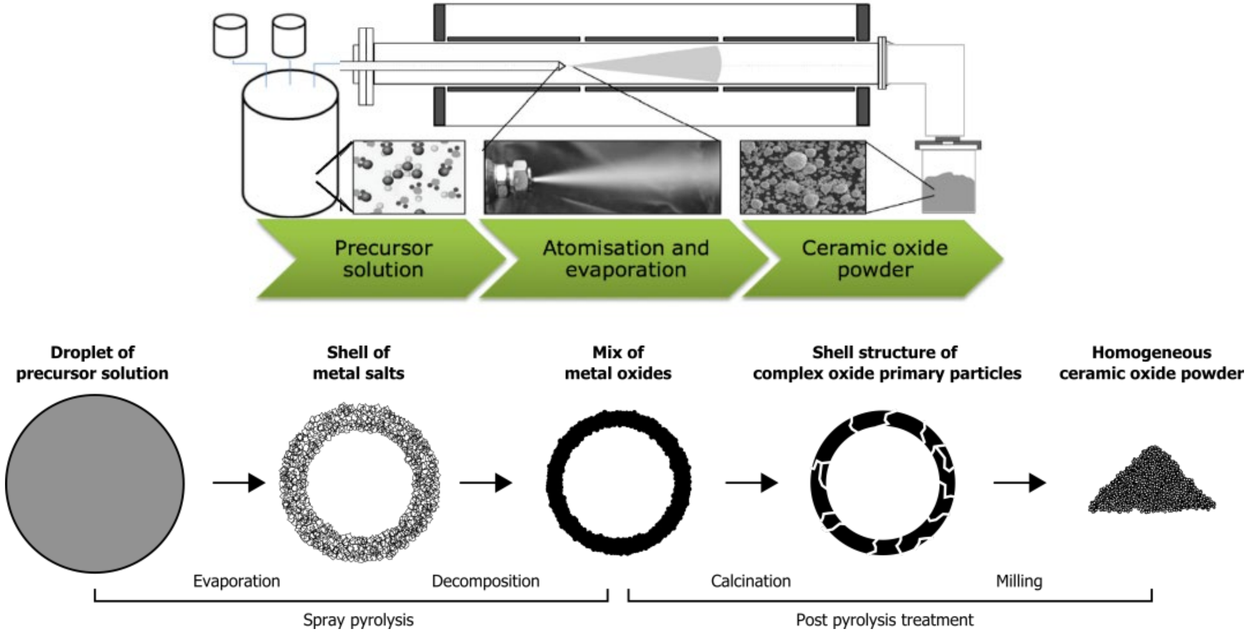
I. Tezsevin J. Phys Chem.Letters **12** 4160 (2021)

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

Oxygen Separation II: Material Production

- Complete process chain from feedstock chemicals to customized powders
- Solution → Continuous Spray Pyrolysis → Calcination → Milling
- **Spray pyrolysis process**
  - Agglomerates of submicron powder with crystallites 10-500 nm
  - Specific surface area in the range of 1-50 m^2/g
  - Production capacity: several tons per year

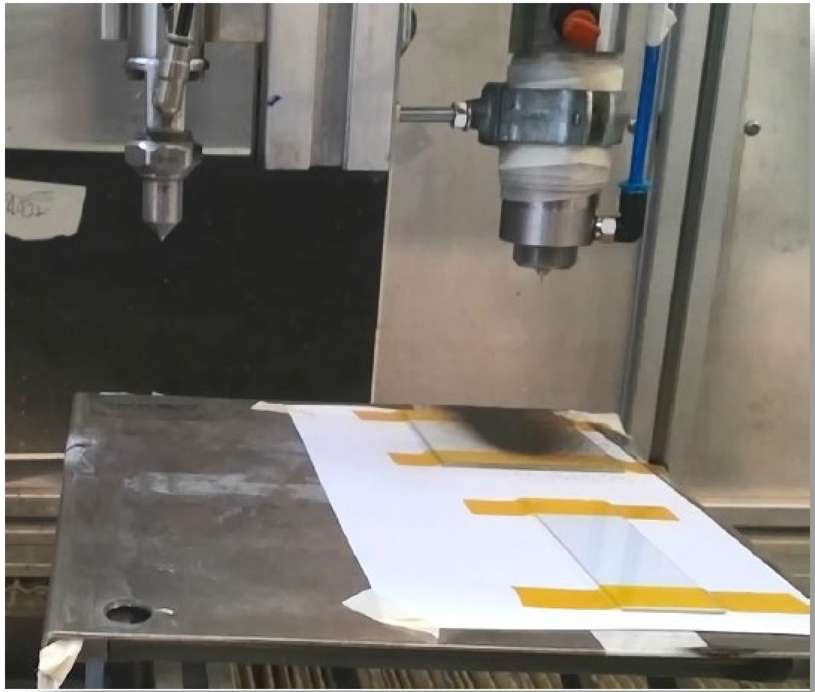




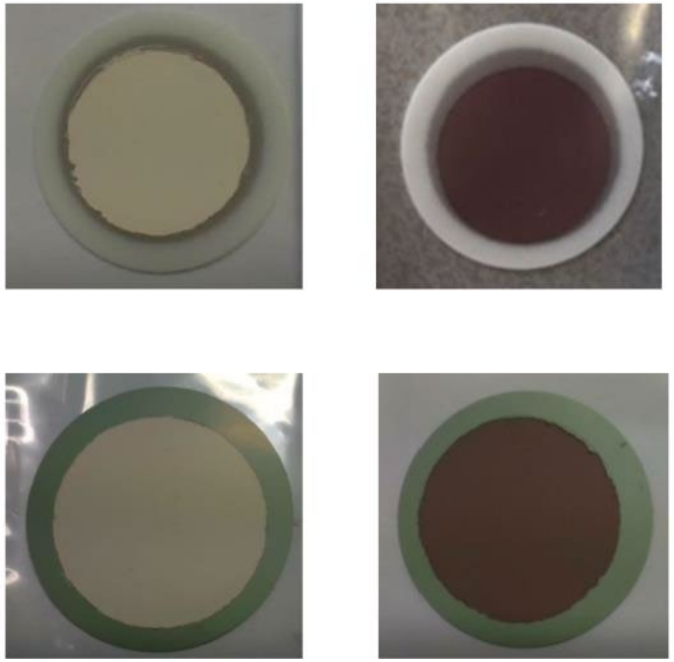
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Oxygen Separation III: Material Processing

- Development of an alternative coating methodology for solid oxide cells
- → **Spray coating** instead of traditional tape casting



Spray coating process



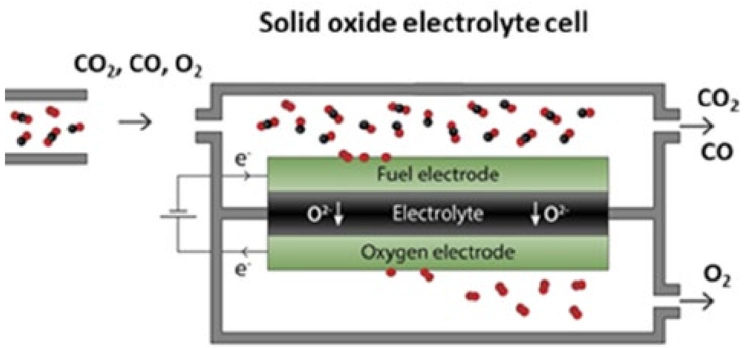
SOE button cells

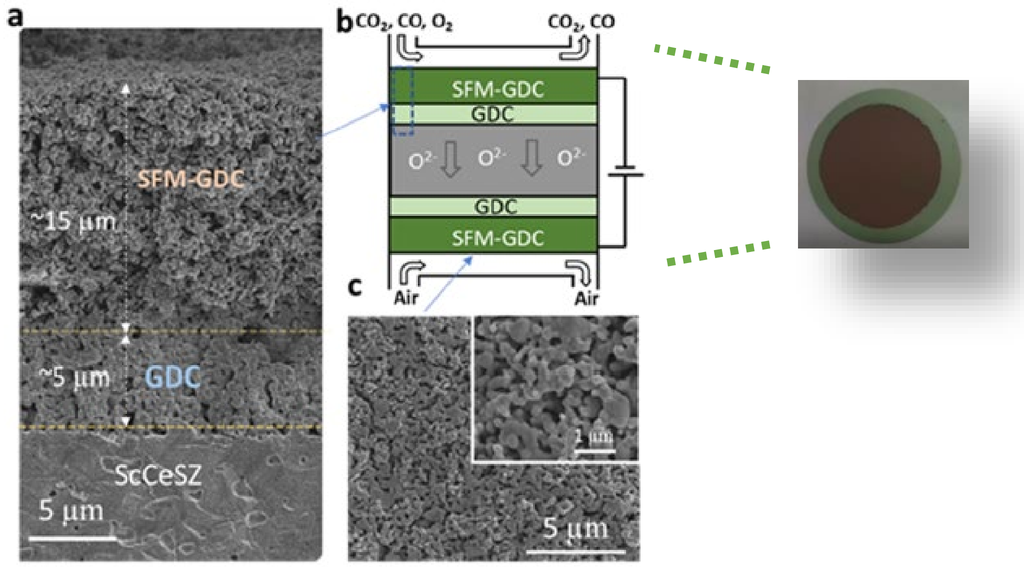
Individual cells before testing

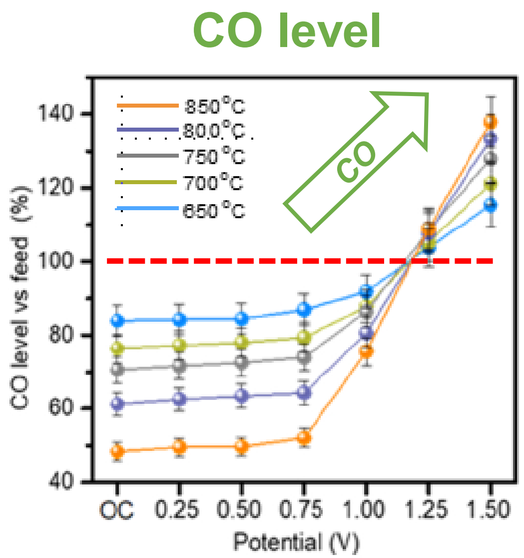
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

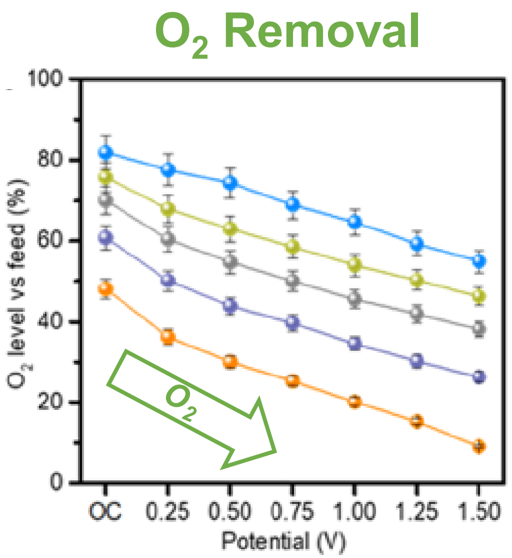
Oxygen Separation IV: Separation performance

- Oxygen removal favoured at increased temperatures
- High Faradaic efficiency observed (> 90%)
- 91% less oxygen when compared to the plasmolysis equivalent feed
- Increased CO production (up to 138% of plasmolysis feed)
- No cell degradation observed for > 100 hours







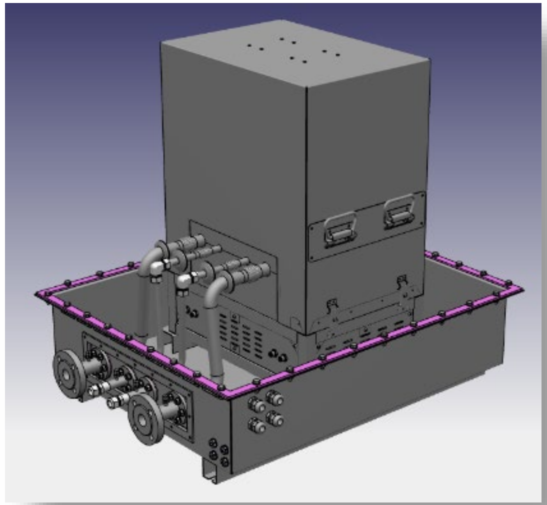


A Pandiyan et al Journal of CO_2 Utilization 57 (2022) 101904

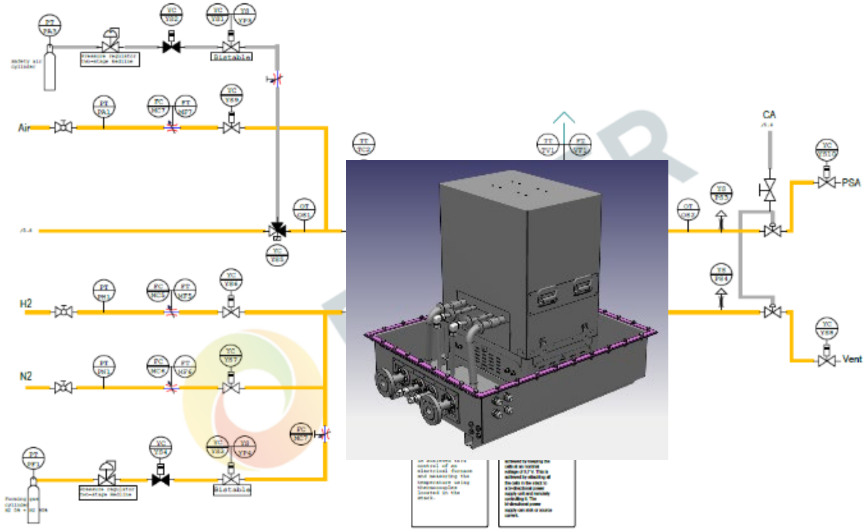
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Oxygen Separation V: Modules @ Technical scale

- Commercial SOE cell stack modified with KEROGREEN electrode materials
- Cell stack equipped with functional technical layer(s)" to accommodate fluctuating gas stream supplied from plasmolysis module
- **Key figures**
    - Surface area: 5600 cm^2 (> 5 Nl/min oxygen removal capacity)
    - 1.5 kW_{el} electrical power equivalent



Modified commercial stack



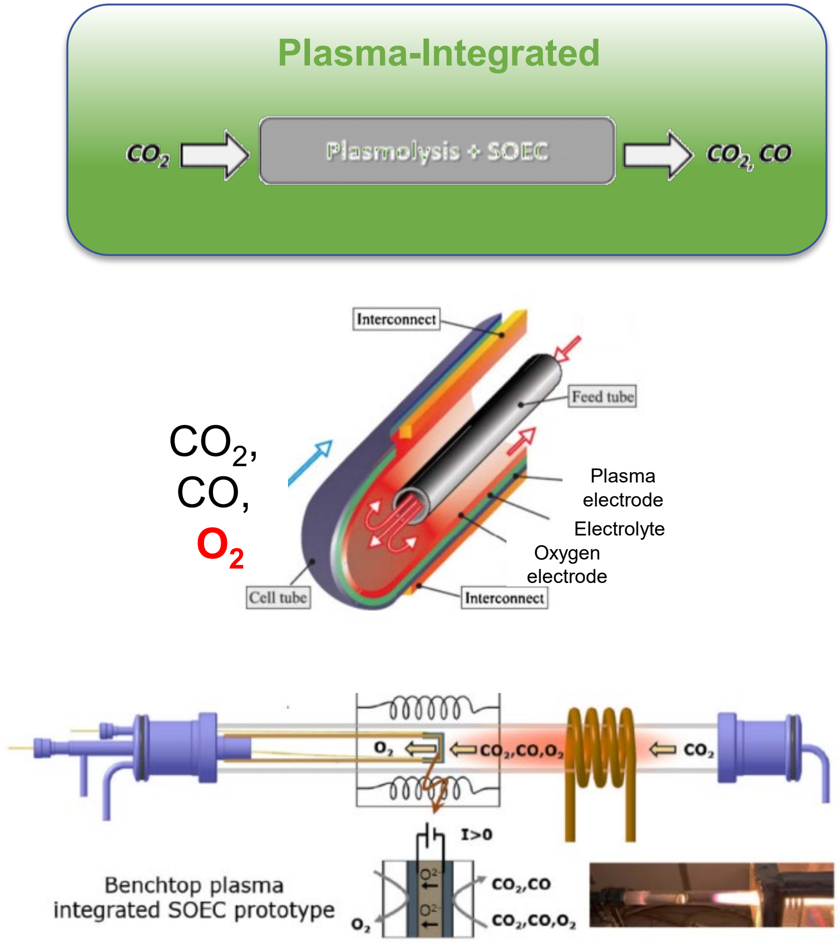
Functional technical layer

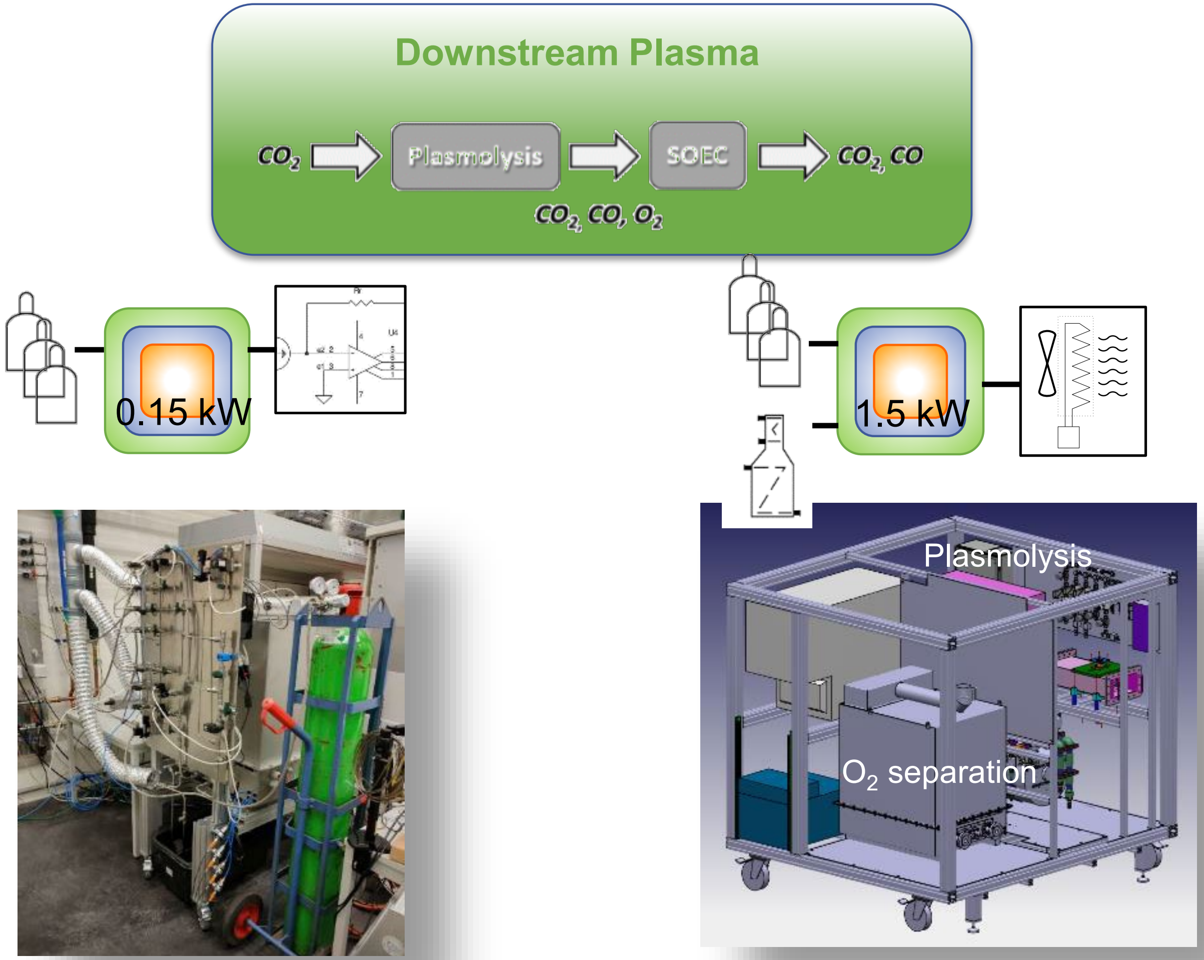
Integrated plasma + separator module

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

Oxygen separation V: Performance Testbenches

Preparation of testbenches for KEROGREEN gas mixture (CO_2 / CO / O_2)

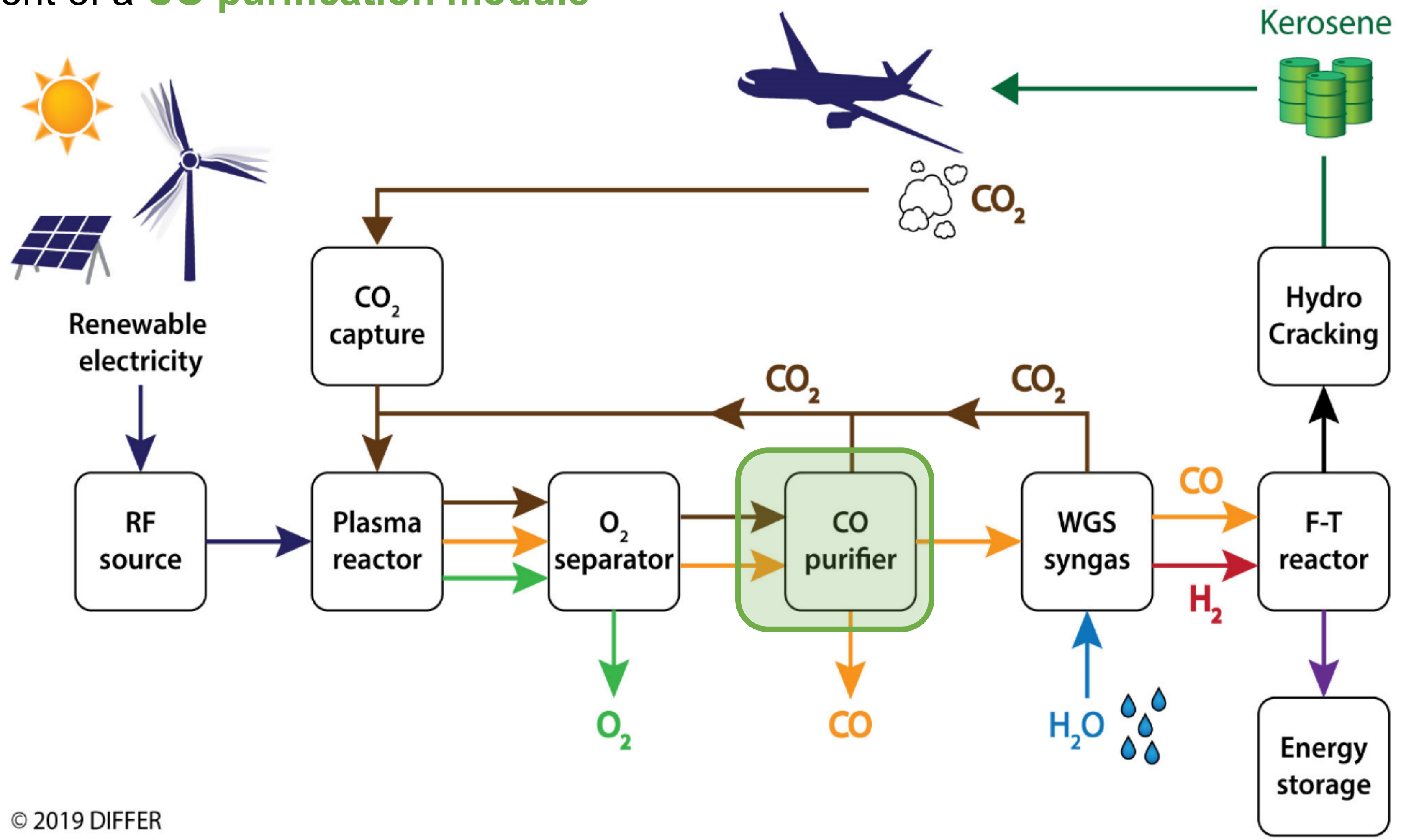




This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Upstream processes

- Development of a **CO purification module**



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

CO purification: Pressure Swing Adsorption

- Modular and scalable purification systems
- From few Nl/min to several thousand Nm^3/h
- Kerogreen lab scale system was assembled and tested

Smaller scale module

***KEROGREEN** lab scale module*

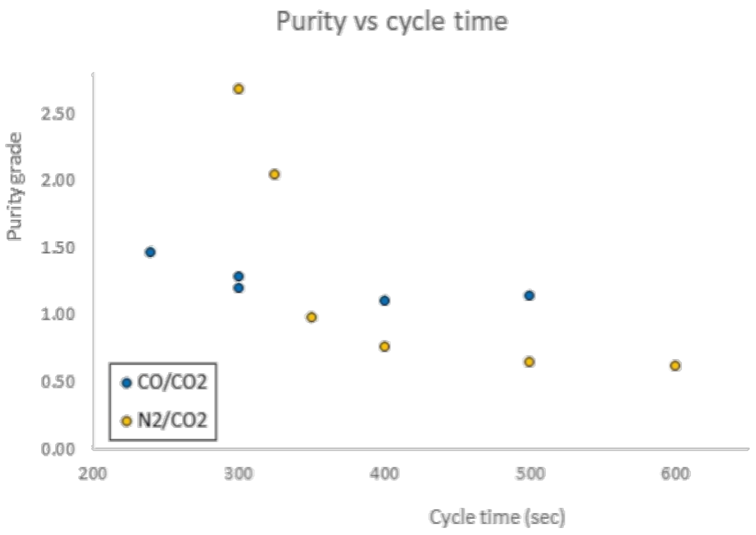
Industrial scale purification module

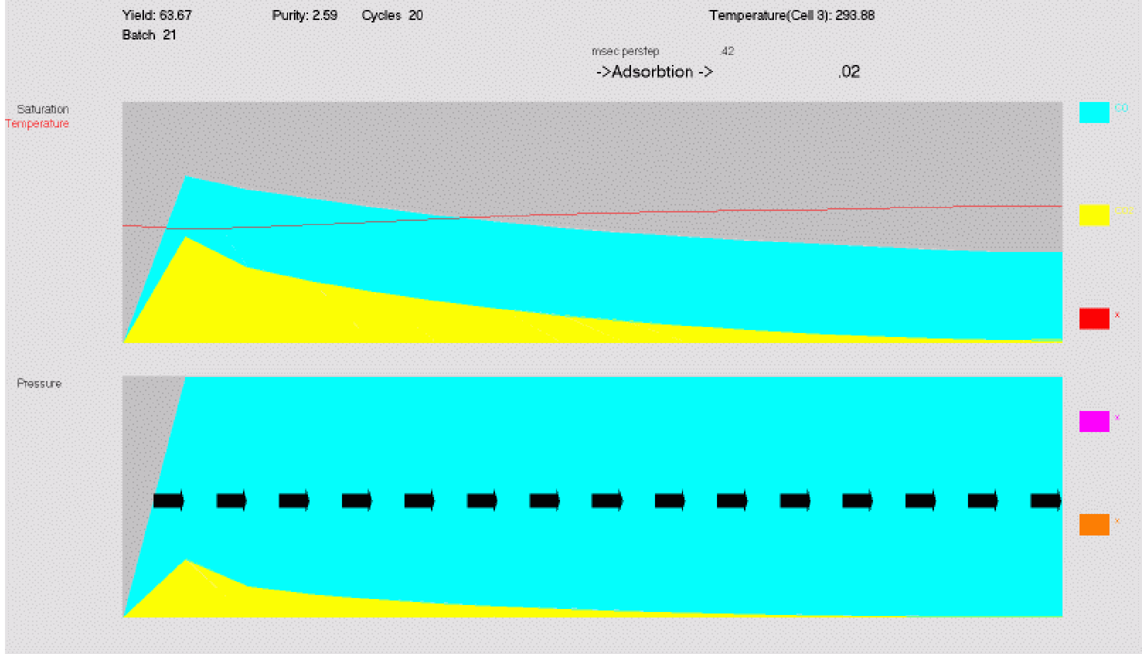
Size of Modules

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

CO Purification Module

- Results from test campaign showed good agreement with model in terms of CO yield
- However the purity grade was overestimated by the model
- For applications where CO purity of 99.6 % is required: modifications to be applied to the commercial scale system: a two-stage system with recirculation
- **Some key numbers**
    - CO yield after purification 78 % at 98 % purity (Target CO yield for industrial scale: 68 % at 96 % purity)
    - Maximum CO yield of 95 % was achieved
    - Maximum CO purity reached was 98.2 %

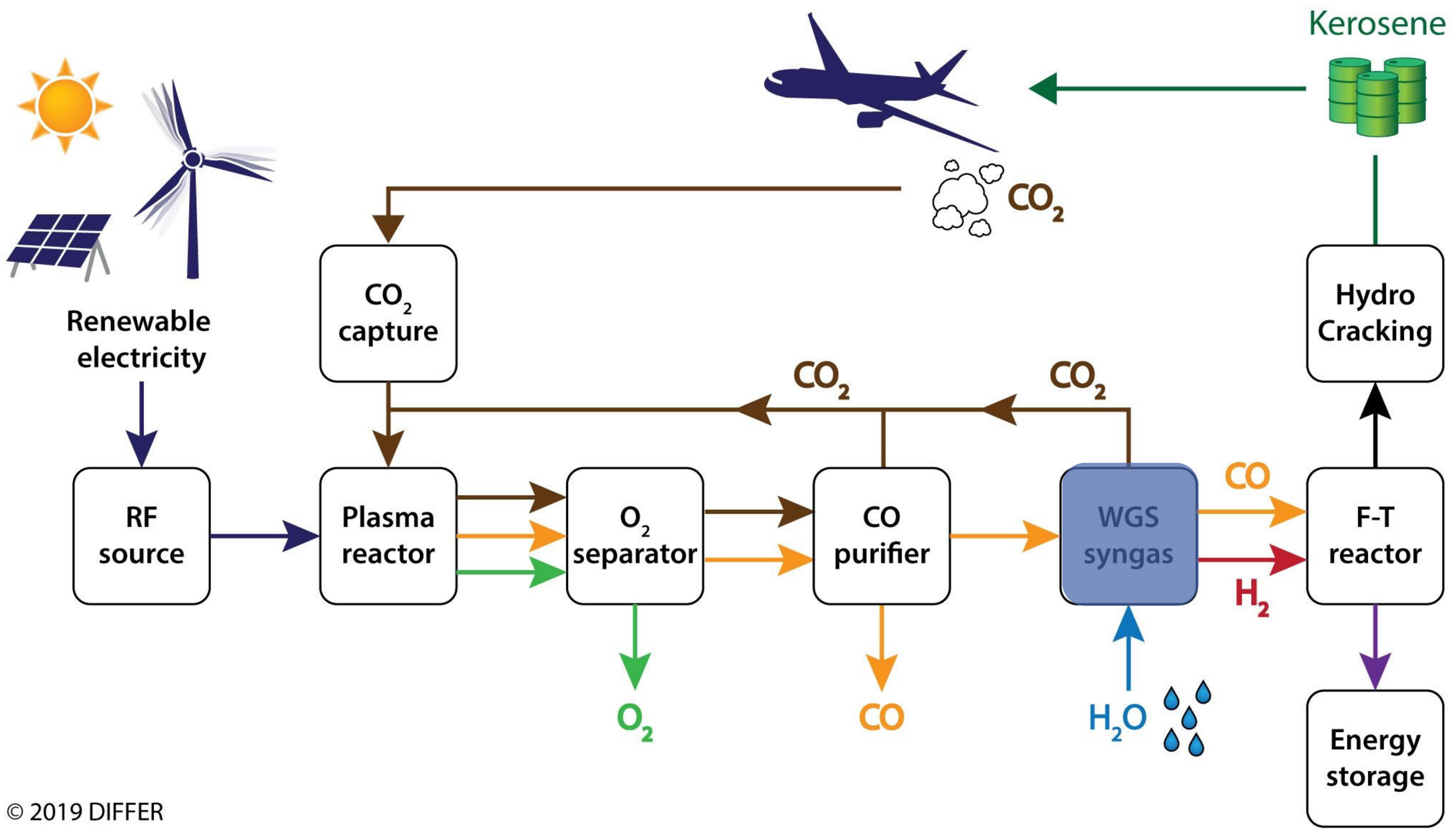




This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Downstream process

- Development of sorption-enhanced water gas shift (SE-WGS)



© 2019 DIFFER

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

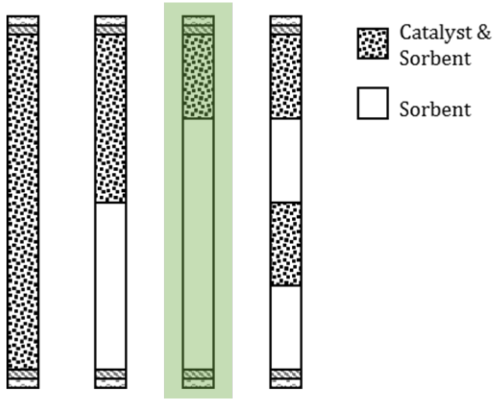
Sorption Enhanced Water Gas Shift (SE-WGS)

- Required to produce synthesis gas ($CO + H_2$) from pure CO
- Combines CO_2 removal from reaction (sent back to Plasma reactor)

$$2\mathbf{H_2O} + 2\mathbf{CO} + (\mathbf{CO}) \rightleftharpoons 2\mathbf{H_2} + (\mathbf{CO_2})_{ads} + (\mathbf{CO})$$

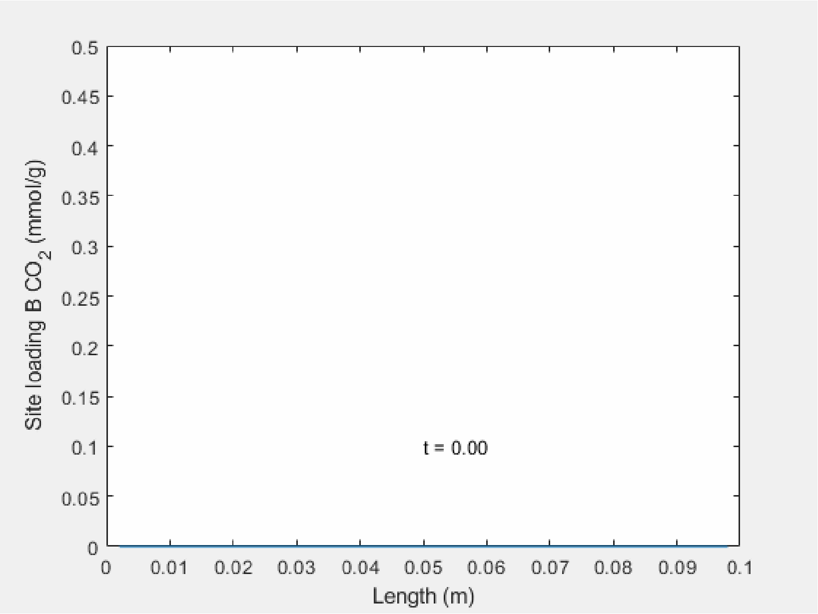
Adsorbed and in cycles desorbed for recovery

- Work started from the scratch in lab
  - effect of pressure
  - effect of steam
  - effect of reactor filling



Catalyst/absorbent configurations tested

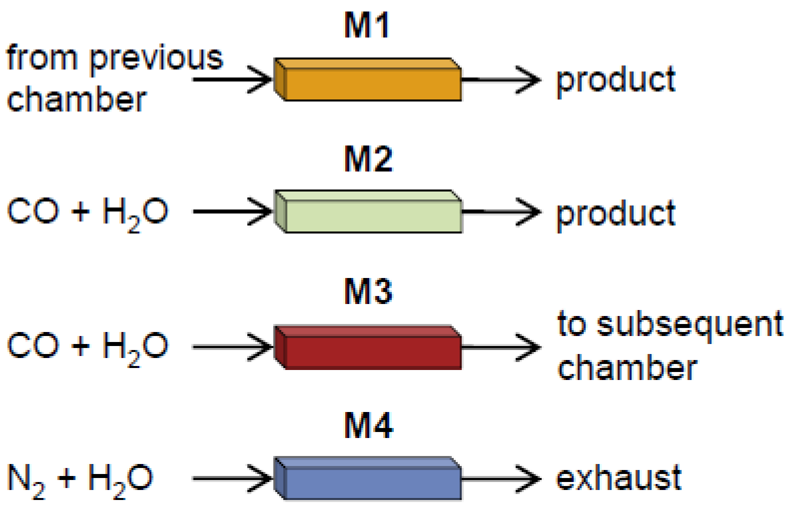
Adorbent loading as function of reactor length

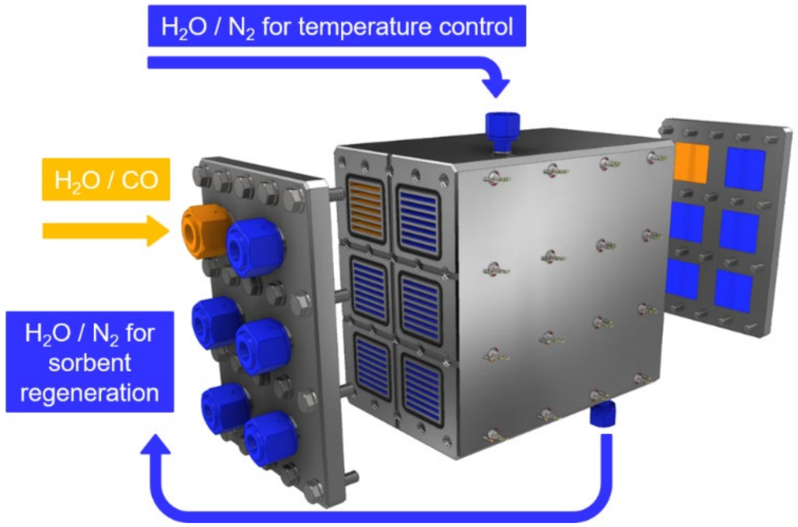


This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

SE-WGS in technical scale @ container site

- Completed reactor design for optimal temperature regulation
- Six chambers in one reactor for switching between reaction & adsorption vs desorption
- Subsequent desorption with steam to avoid impurities in recycled CO_2
- Pre-evaluation of performance by modeling with determined kinetics suggests a four step operation, which is programmed along with two step operation (M2-M4) for each of the chambers



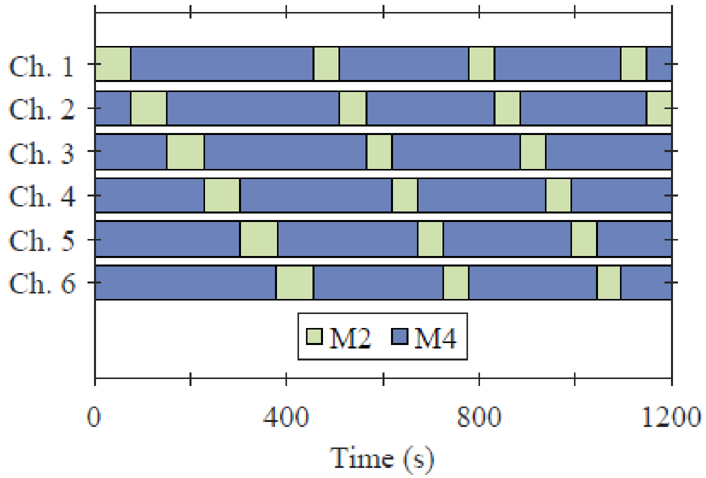


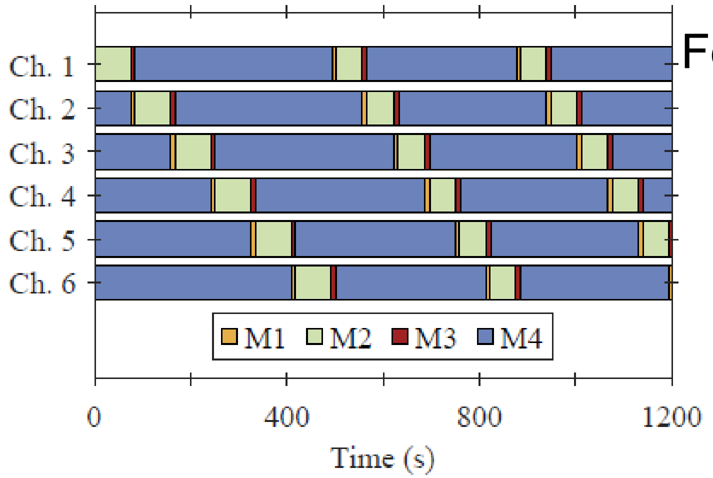
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

SE-WGS in technical scale @ container site

- Implementation in operational scheme and build-up of SE-WGS skid

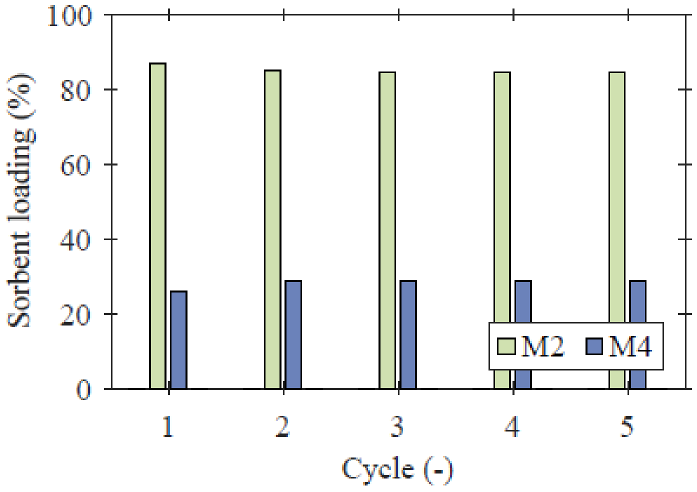
Two steps

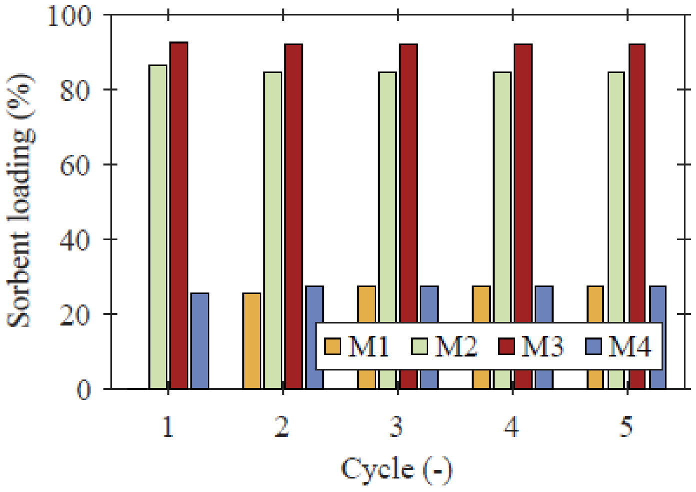




Four steps

- Much more sorbent loading at four steps (more efficiency)



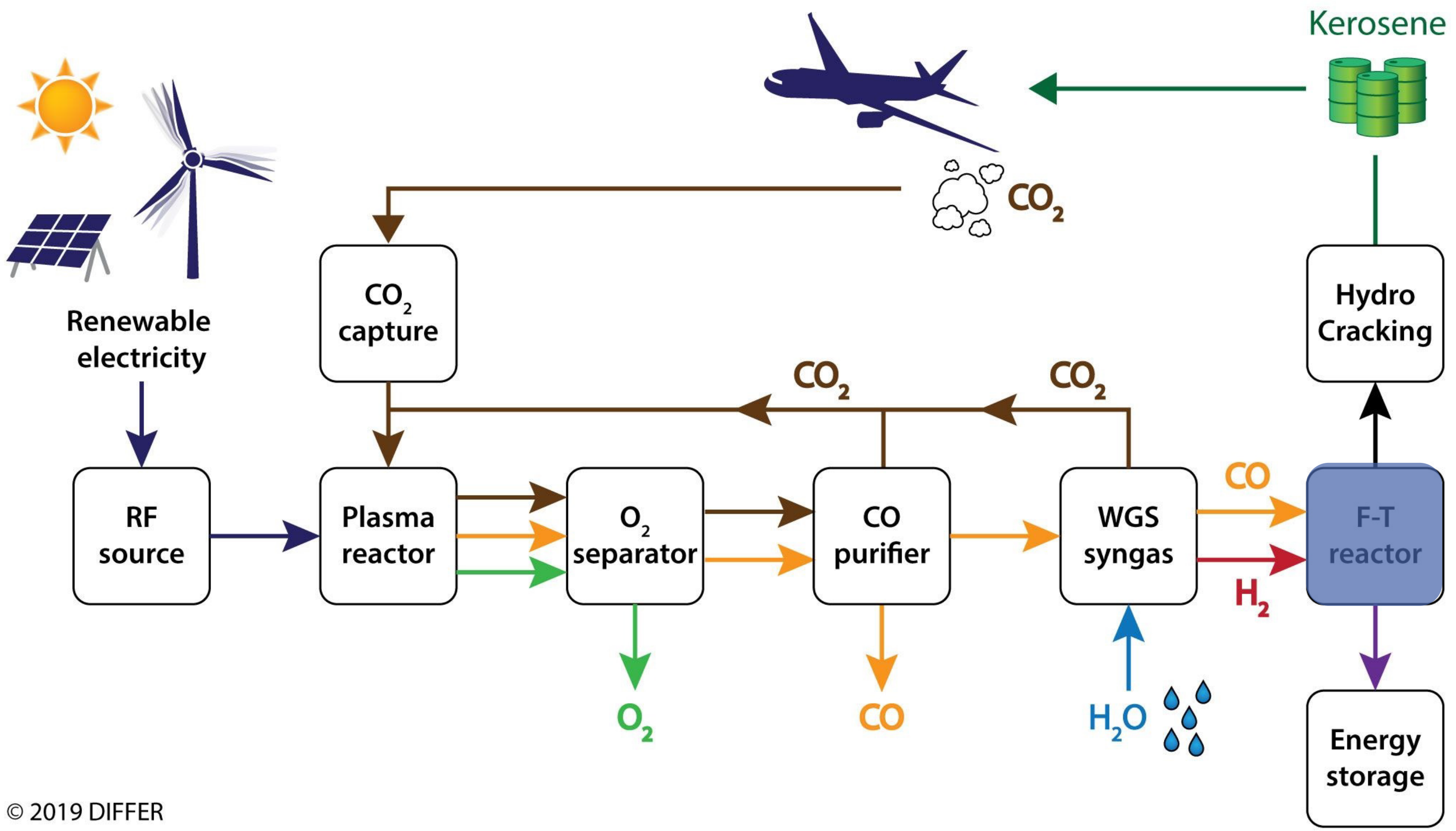


- … to be validated!

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

Downstream process

- Development of Fischer-Tropsch module

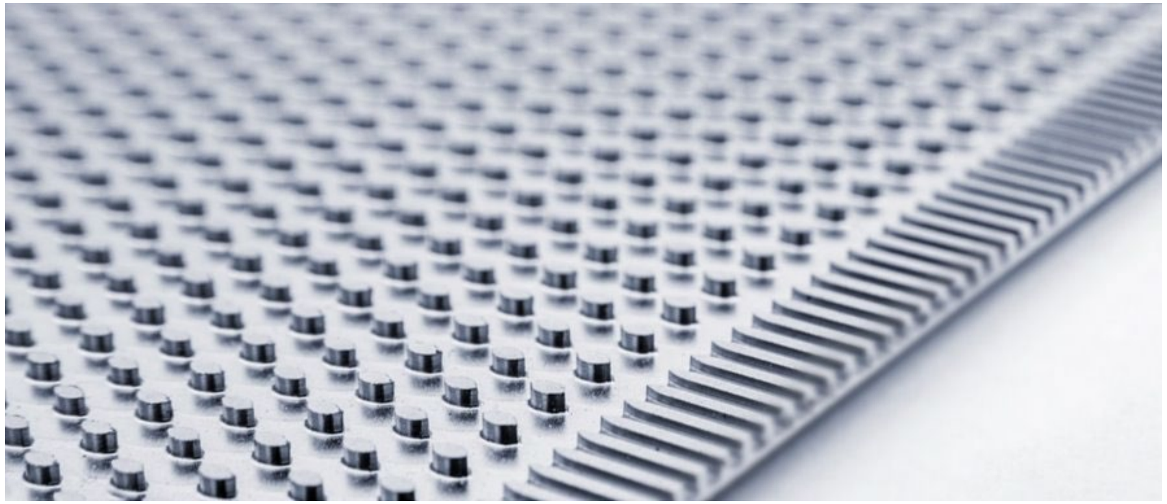


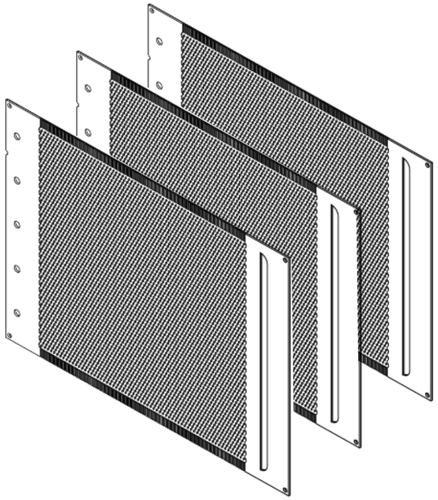
© 2019 DIFFER

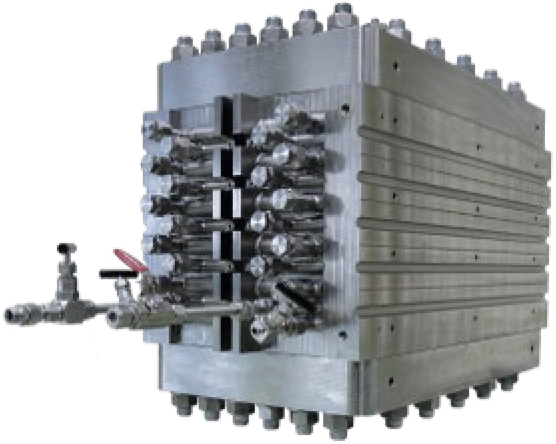
This project has received funding from the European Union‘s Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

INERATEC's Fischer-Tropsch technology

- INERATEC's Fischer-Tropsch reactors are based on modular microchannel technology, thus
  - Reaction temperature can be controlled precisely / safe operation
  - Ramp-up & load changes are possible in minutes, not in days like standard technology (slurry bubble column reactors)
  - High conversion per pass & consequently low process complexity
  - Factor 80 in volumetric process intensification





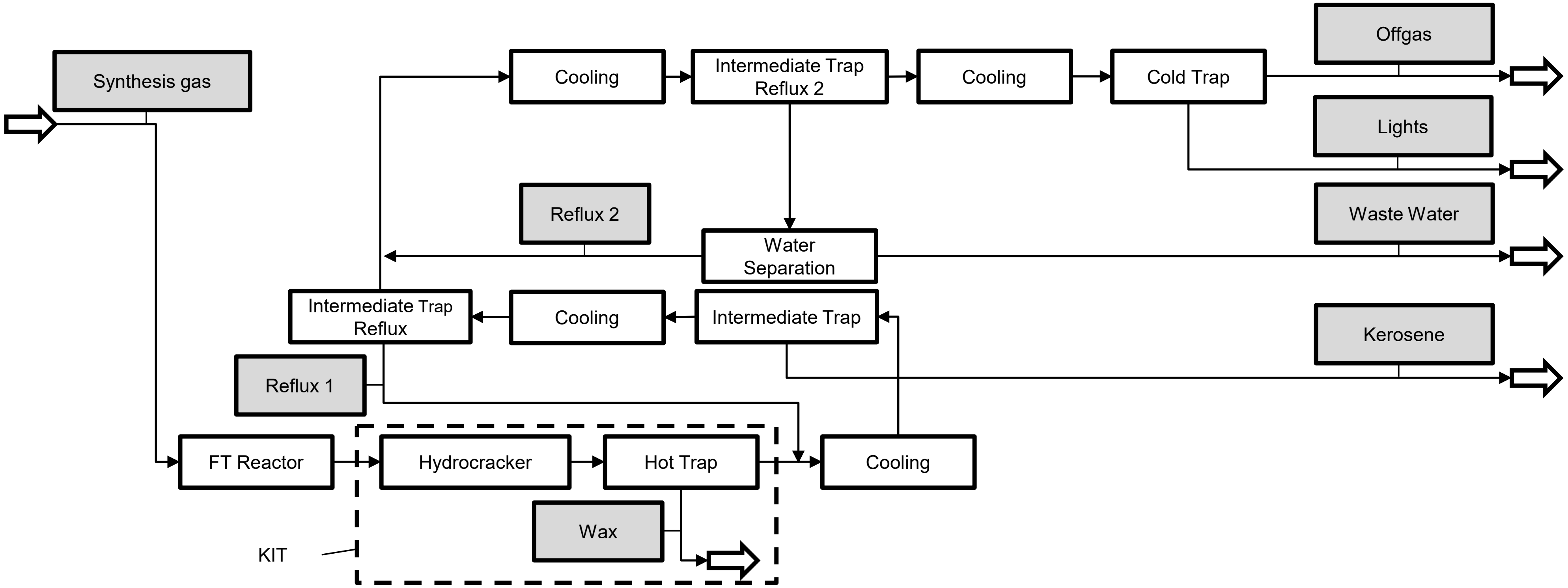


FT module (up to 1,25 MW capacity)

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

What was built?

- A Fischer-Tropsch Synthesis unit with 3 stages of separation
- The waxes are recycled from hot trap to the hydrocracking unit (cooperation with KIT)

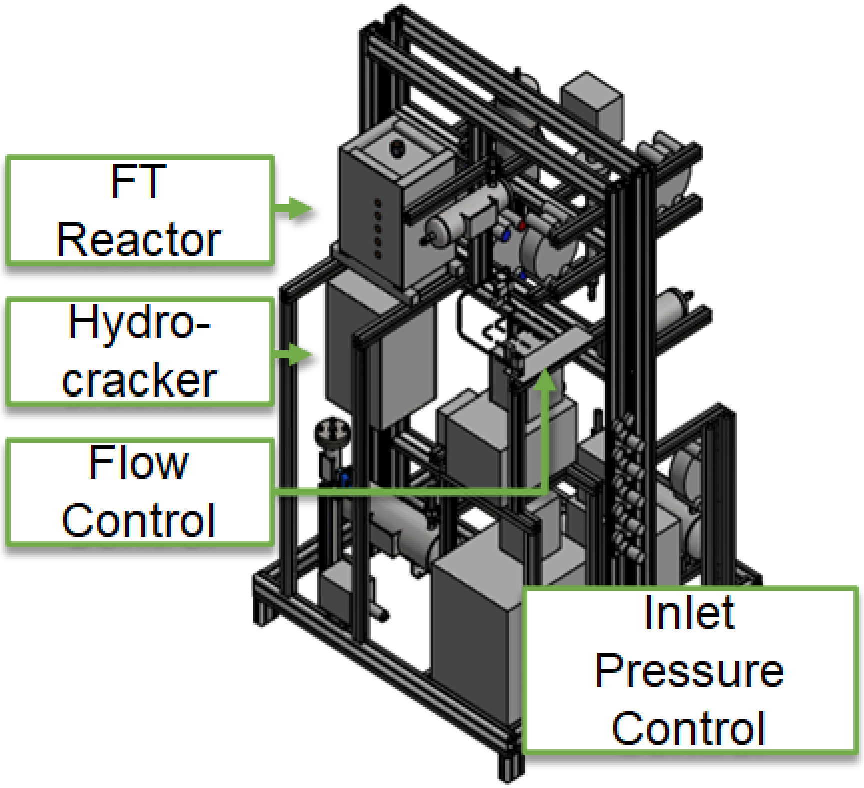


This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Results from Fischer-Tropsch campaigns

- Stable reaction zone temperatures achieved because of stable inlet volume flows
- It was managed to produce 0,11l/h of liquid products
- The results confirm nicely the simulations the plant was based on
- Contamination of O_2 has effects on process and catalyst e.g., 1% O_2 reduces CO conversion from 44% to 28% -> High limit for O_2: 200 – 500 ppm

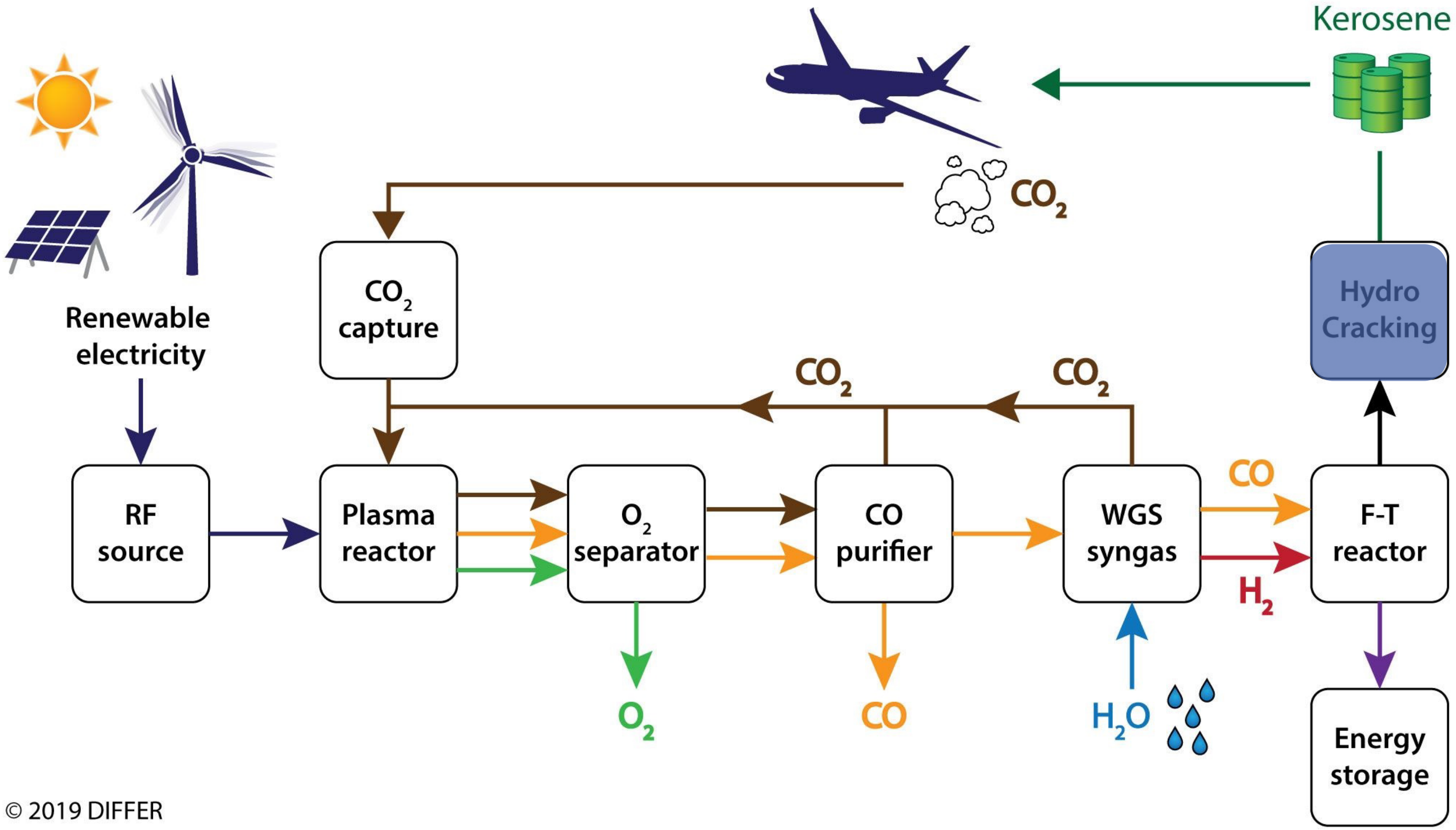
- Outlook:
  - Currently, INERATEC has built two 1MW plants and is in commissioning phase
  - Further, INERATEC is working on a plant with a capacity of 3500t/a in cooperation at Industriepark Höchst in Frankfurt



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

Downstream process

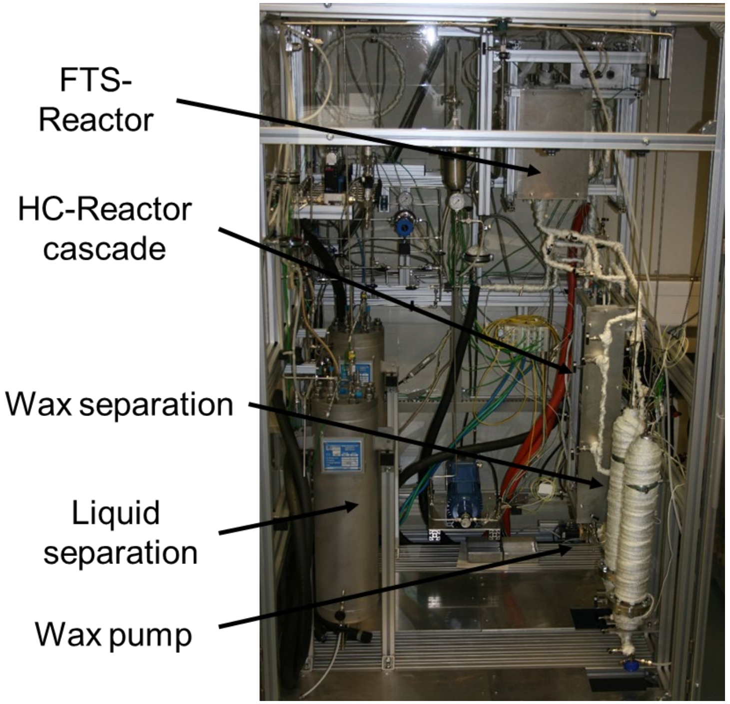
- Development of individual modules



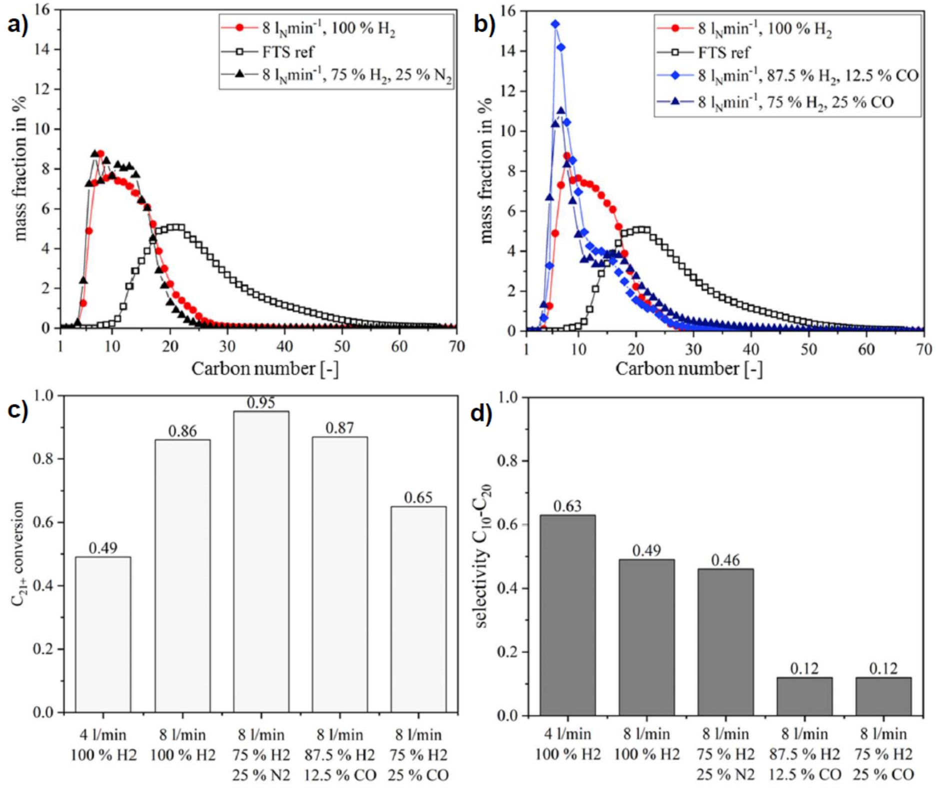
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Hydrocracking to increase Kerosene yield

- In addition to adapt properties (increase yield of species for cold-flow properties)
- "Cut" of long chains (solids at room temperature) from Fischer-Tropsch synthesis towards hydrocarbon molecules C_8-C_{14} (Kerosene fraction)
- Started from pre-existing lab scale setup:



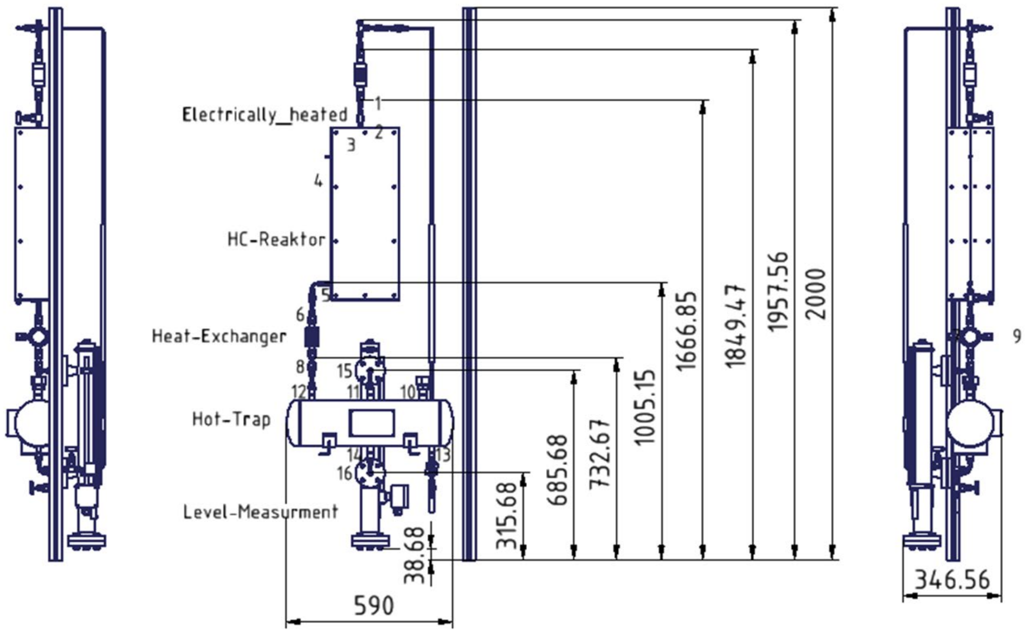
Trade-off between conversion of long chains (C_{21+}) and selectivity to hydrocarbons C_{10}-C_{20}



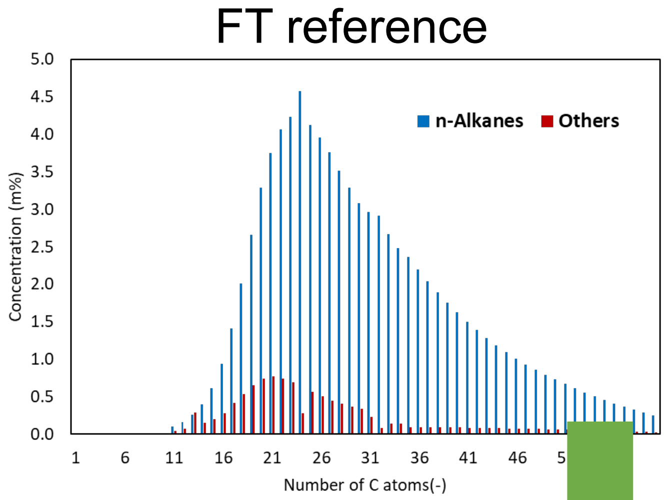
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

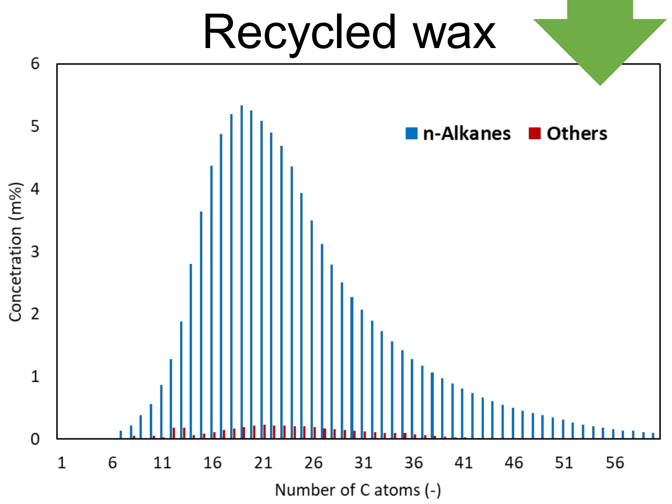
HC integration into FT-synthesis skid

- With wax recycling from hot trap (wax condensation) back to the hydrocracking reactor which is located directly behind the Fischer-Tropsch reactor
- Avoids partially the typical trade-off by covering the catalyst with liquid and thus reduces overcracking
- Only ~2 kg residual wax in the whole campaign



Proof of wax recycling due to cleaning effect (only paraffins left over)

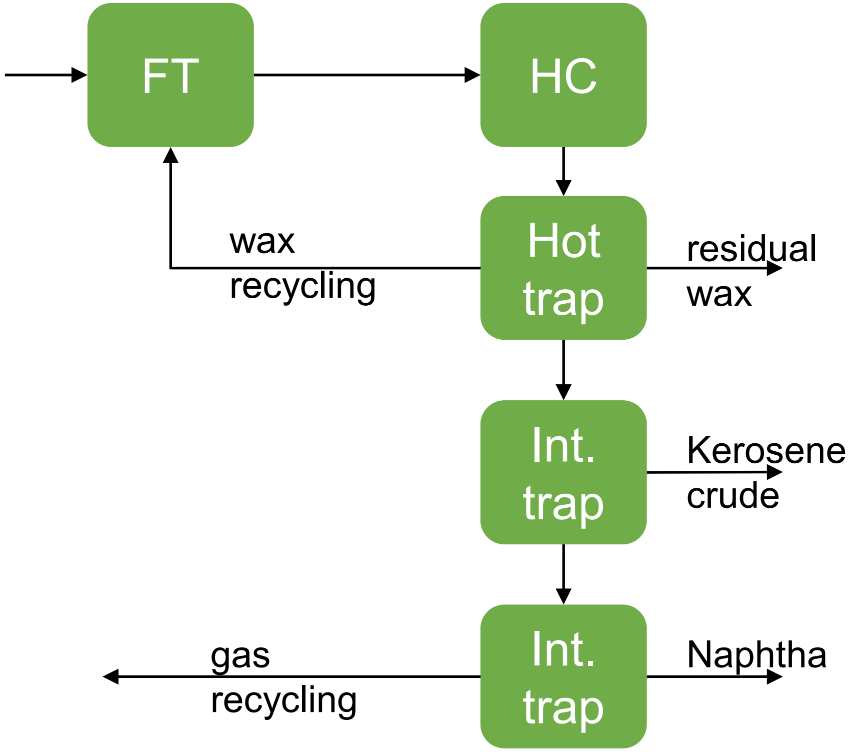




This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

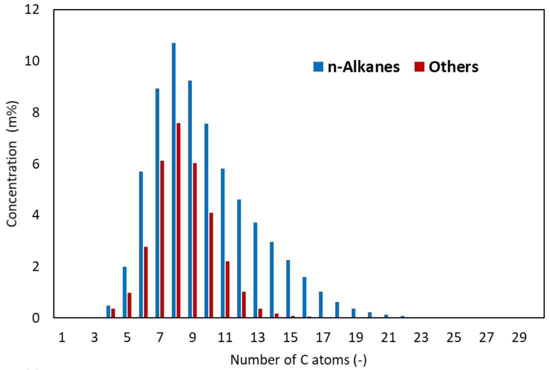
HC integration into FT-synthesis skid

- Hydrocracking performance increases with increased HC temperature and wax recycling i.e., „others“ (isomers after further hydrogenation upgrading) content increases in both the intermediate and cold trap
- Pre-condition for successful upgrading towards Kerosene reached

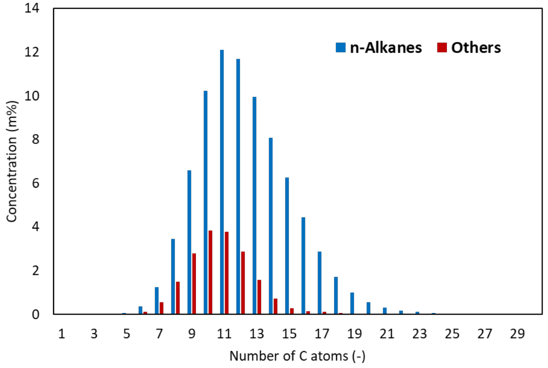


HC (283°C,
2 ml/min
recycling)

Cold trap



Intermediate trap



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

Full process integration

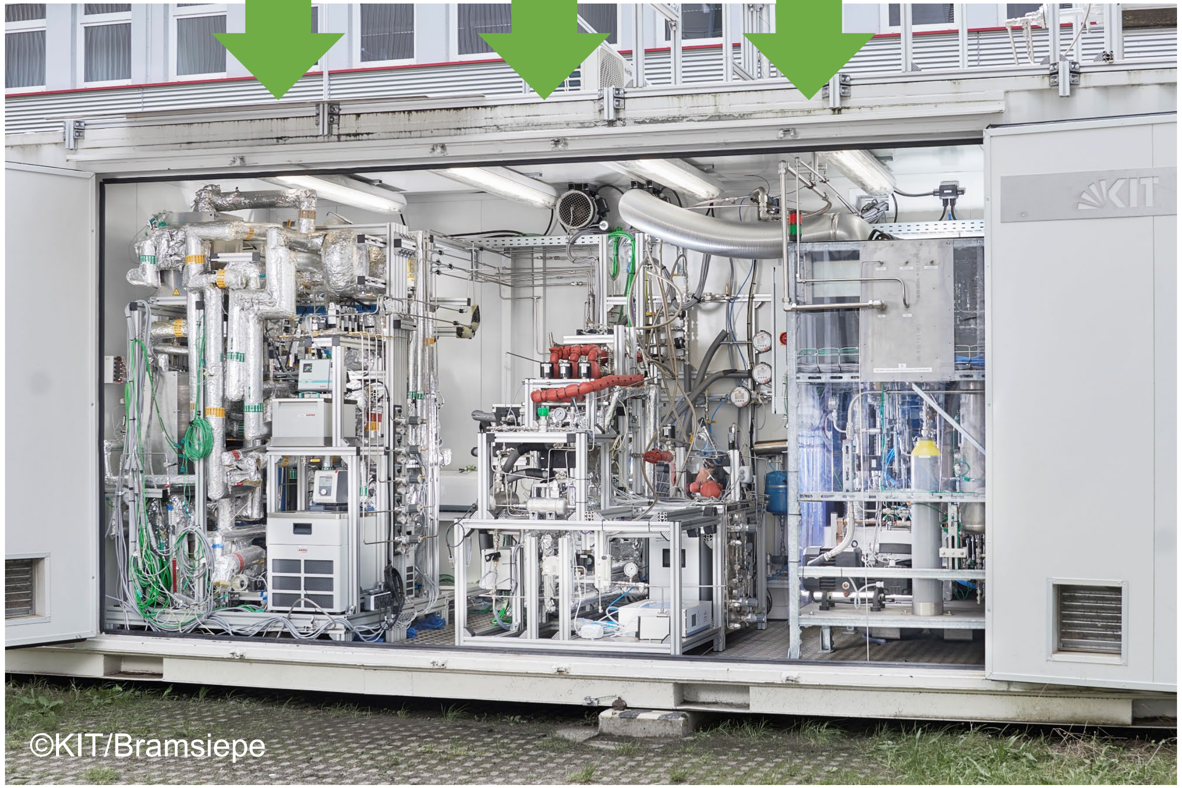
- Completed in the final months of the project duration

DIFFER

FT & HC — INERATEC

SE-WGS — KIT Karlsruhe Institute of Technology

CO-Purification — KIT Karlsruhe Institute of Technology, HYGEAR



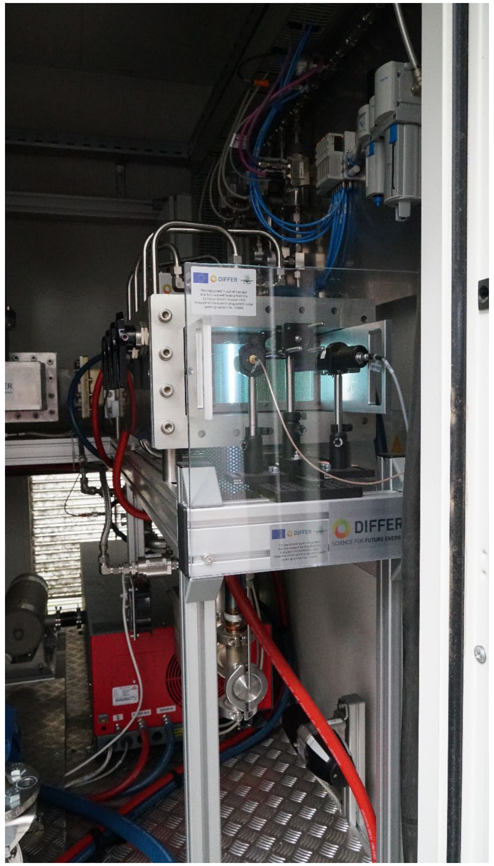
O_2-Removal — Cerpotech, HYGEAR, vito, DIFFER

Plasma — DIFFER

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

Validation of integration

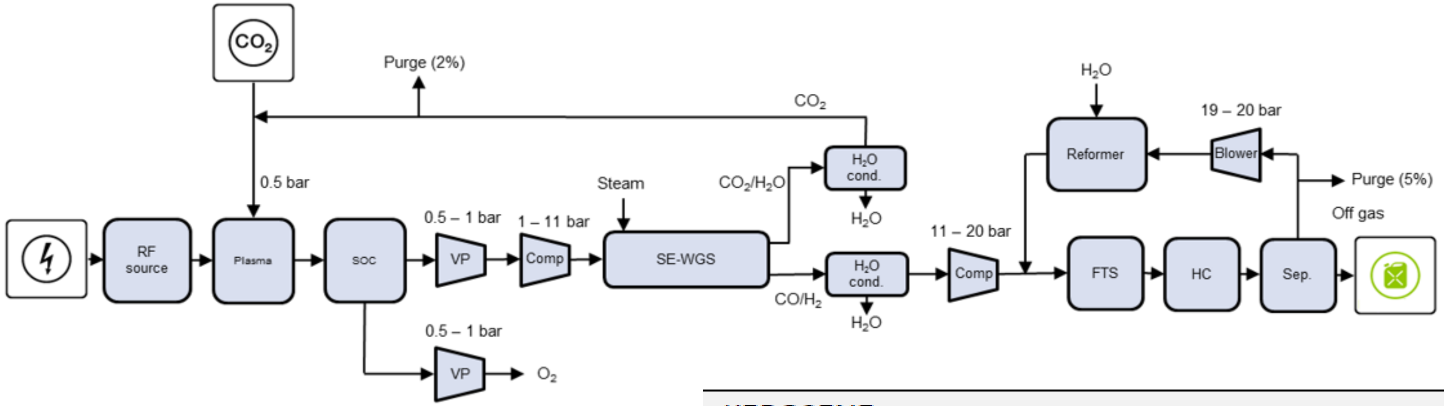
- e.g., test run plasma completed



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

Calculation of process efficiency

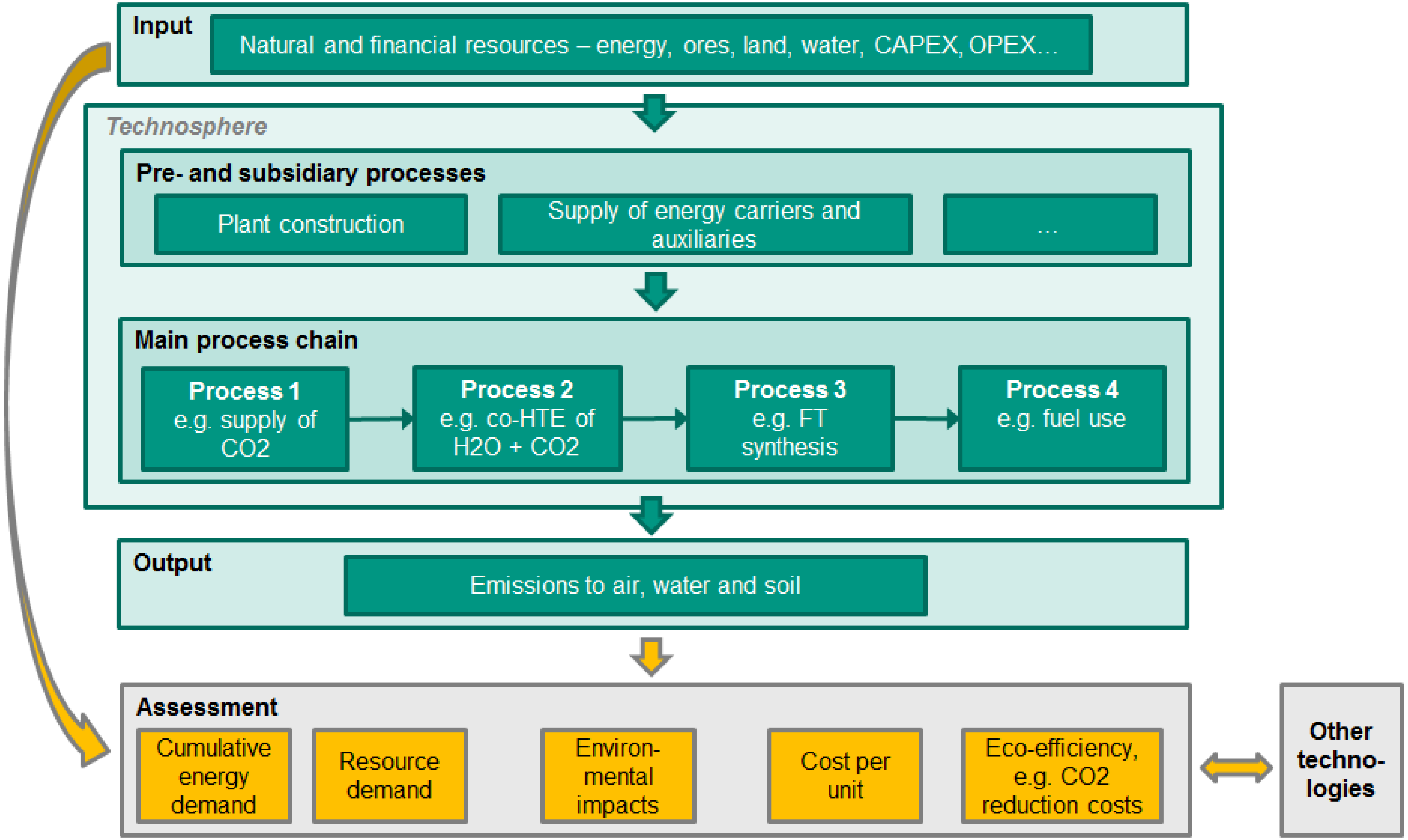
- Applied process and model scheme in commercial software Aspen® & Matlab Simulink®
- CO_2 efficiency ($X_{CO_2} = \frac{\dot{V}_{Synthesis\ Gas}}{\dot{V}_{CO_2,Feed}}$, before FT reactor) is 17% => all CO_2 needs to be recycled!
- At 40 l(N)/min CO_2 a Kerosene output of 0.042 kg/h is produced in single pass
- Full CO_2 recycling needs to be implemented on industrial scale



KEROSENE		
AMOUNT	g/min	0.7
DENSITY	kg/m³	774.0
T95	°C	411.0
VOLATILES	wt-%	0.6
OFFGAS	NL/min	2.3

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

Sustainability assessment



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

Sustainability assessment

KIT Karlsruhe Institute of Technology

Goals

Ranking of KeroGreen and competitors
=> Identification of performance requirements

Improvement of KeroGreen
=> Fulfilling of performance requirements

Methods

Environmental aspects: Life Cycle Assessment (LCA)

Economic aspects: Life Cycle Costing (LCC)

Social aspects: s(ocial)LCA - numerous approaches => Indicator: Acceptability

Generally: competing technologies with numerous pros and cons & our technology in early stage

An example: results for GHG emissions

- benefits from KeroGreen only in case of pure renewable power generation with high mean loads and full use of by-products; also in future limited potentials for on-shore power production in middle Europe
- only small differences among the four investigated concepts
- similar pattern for other impacts e.g., eutrophication or particle matter formation

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

Karlsruher Institut für Technologie

Thank you for your attention!

…buy SAF and do CO_2 compensation, when you fly…

…or go by train!

Contacts

Dr. Stefan Welzel
Dutch Institute for Fundamental Energy Research (DIFFER)
Solar Fuels - Facilities & Instrumentation
De Zaale 20
5612 AJ Eindhoven, The Netherlands
s.welzel@differ.nl
+31.(0)40.3334.770

Prof. Peter Pfeifer
Karlsruhe Institut für Technologie
Institut für Mikroverfahrenstechnik
Hermann-von-Helmholtz-Platz 1
76344 Eggenstein-Leopoldshafen
peter.pfeifer@kit.edu
+49 (0) 172 3604443

KEROGREEN

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