KEROGREEN Winter school

Future directions in research on Power-to-X for sustainable chemicals & fuels

10-11 February 2022

in collaboration with E-Fuel, BECCU and EERA JP Energy Storage

KEROGREEN has received funding from the European Union‘s Horizon 2020 Research and Innovation Programme under grant agreement No 763909.

Towards sustainable and green aviation fuel production

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Online event (Zoom)
Chair: Prof. Roland Dittmeyer, Karlsruhe Institute of Technology, DE

KEROGREEN is a Research and Innovation Action (RIA), financed by the European Commission under the Call Topic “Competitive low-carbon-energy - new knowledge and technologies” (H2020-LCE-06-2017) in the H2020 Work programme “Secure, Clean and Efficient Energy”.

The main goal of this project is the development and testing of an innovative conversion route for the production of sustainable aircraft grade Kerosene from water and air powered by renewable electricity. The KEROGREEN conversion route is based on plasma driven dissociation of air captured CO_2, solid oxide membrane oxygen separation and Fischer-Tropsch (F-T) kerosene synthesis.

The winter school was **organised together with** the research projects **E-Fuel** and **BECCU** and the **EERA Joint Programme Energy Storage** (EERA JPES). It provided the latest developments on the Power-to-X related technologies and their future directions. Especially concepts aiming at ensuring sustainability have been pointed out. Topics like CO_2 capture, Electrolysis, Co-Electrolysis, Chemical synthesis, Plasmolysis, Fuel synthesis, System integration and System, process, reactor and kinetic modelling have been addressed.

The event gave the opportunity to young researchers to present their research activities and results in either short talks or posters. It also included a special session (with a contest) dedicated to presentations from doctoral students from the EERA JPES network (EERA PhD day).

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PROGRAMME

Thursday 10th February 2022

9:00 – 9:10	**Opening Winter school and Welcome (R. Dittmeyer)**
	Chair morning session: *Juha Lehtonen, VTT*
9:10 – 9:35	**EU Project KEROGREEN: Main Challenges and first results** Adelbert Goede, DIFFER (NL)
9:35 – 10:00	**Plenary presentation of E-Fuel and BECCU Projects** Juha Lehtonen, VTT (FI)
10:00 – 10:25	**Status of modular plants for decentralised Power-to-X** Michael Rubin (Klumpp), KIT (DE)
10:25 – 10:45	**Coffee break**
10:45 – 12:05	**Oral presentations** – Vanesa Gil, Aragon Hydrogen Foundation: Air Carbon Recycling for Aviation Fuel Technology – Jan-Willem Könemann, TNO: Take-Off a novel process to synthetic aviation fuel – Christian Frilund, VTT: CO_2 conversion to hydrocarbons using reverse water gas shift and FT-synthesis – Esperanza Ruiz, CIEMAT: Process intensification for advancing Power-to-Fuel
12:05 – 13:05	**Lunch break**
	Chair afternoon session: *Francisco Vidal Vázquez, KIT*
13:05 – 14:05	**Oral presentations** – Mihalis Tsampas, DIFFER: Synergistic combination of plasma and electrocatalysis for nitrogen fixation by water – Stefan Welzel, DIFFER: CO_2 plasmolysis in the KEROGREEN process chain: Development of a plasma reactor module for CO production – Marijke Jacobs, VITO: Development of thin electrode layers by spray coating for solid oxide cells
14:05 – 14:25	**Coffee break**
14:25 – 15:45	**Oral presentations** – Marjut Suomalainen, VTT: Techno-economic assessment of producing diesel from CO_2 and H_2O via co-electrolysis and Fischer-Tropsch synthesis – Vafa Järnefelt, VTT: The potential of CCU technologies in mitigating climate change – Miia Nevander, VTT: Techno-economics of the synthesis route from CO_2 and clean H_2 to polycarbonate polyols – Joachim Falkenhagen, Windland Energieerzeugungs GmbH: Green Future Quota" for power-to-X fuels like green hydrogen and kerosene
16:00	**End of 1st day**

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PROGRAMME

Friday 11th February 2022

9:00	**Start 2nd day**
	Chair morning session: *Roland Dittmeyer, KIT*
9:00 – 9:30	**Invited plenary presentation: The role of hydrogen and hydrogen-derived fuels in the IEA Net Zero Emissions 2050 roadmap** Ilkka Hannula, IEA (FR)
9:30 – 10:50	**Oral presentations** – Emil Drazevic, Arhus University: Decentralized production of green and sustainable ammonia – insights from EU/Japan collaboration – Onni Linjala, VTT: CO_2 supply options for P2X and results from carbon capture experiments – Sari Rautiainen, VTT: Fossil-free polycarbonate polyols from captured carbon dioxide and renewable hydrogen – Dorela Dhamo, KIT: Defossilizing the aviation sector with synthetic fuels (poster)
10:50 – 11:10	**Coffee break**
11:10 – 12:30	**Oral presentations** – Peter Holtappels, DTU: Organic Electrosynthesis: a sustainable route to polymers and other high value chemicals? – Mikko Lappalainen, VTT: State-of-the-art and future mapping of electrolyser technologies – Ville Saarinen, VTT: High temperature electrolysis and co-electrolysis for production of green hydrogen and syngas – Mery Hernandez, KIT: Plasma assisted H_2O_2 synthesis from water and oxygen
12:30 – 13:30	**Lunch break**
13:30	**EERA JP Energy Storage “PhD day”**
	Chair afternoon session: *Adelbert Goede, DIFFER*
13:30 – 13:40	**Introduction to the session** Adelbert Goede, DIFFER (NL)
13:40 – 15:00	**Oral PhD presentations** – Tabea Stadler, KIT: Syngas Production in the Kerogreen Process Chain: Development of a compact Sorption-Enhanced Water-Gas Shift Reactor – Georgios Sakas, LUT University: Dynamic energy and mass balance model for an industrial alkaline water electrolyzer plant process – Aki Braunschweiler, VTT: Light olefin production from CO_2 – Manuel Andresh, KIT: Quantitative model-based assessment of global socio-ecological challenges and opportunities for the transition to Power-to-X: Case study for the aviation sector
15:00 – 15:20	**Coffee break**
15:20 – 15:40	**Virtual visits to research infrastructures** (KIT, VTT)
15:40 – 15:50	**AWARD decision**
15:50 – 16:00	**Closing words of PhD day & Winter school (A. Goede, R. Dittmeyer)**

This project has received funding from the European Union‘s Horizon 2020 Research and Innovation Programme under grant agreement No 763909.

Winter school Organisation Committee

KEROGREEN representatives (main organisator):
Roland Dittmeyer (KIT)
Sabine Müller (KIT)
Francisco Vidal Vázquez (KIT)

BECCU & E-Fuel representatives:
Janne Karki (VTT)
Juha Lehtonen (VTT)
Matti Reinikainen (VTT)
Heidi Saastamoinen (VTT)

EERA JP Energy Storage representative:
Adelbert Goede, DIFFER

EERA PhD Day Selection Committee

Emil Drazevic (Aarhus University)
Adelbert Goede (DIFFER)
Peter Holtappels (DTU)
Esperanza Ruiz Martínez (CIEMAT)

Winner of the EERA PhD Day Award

(Payment of Open Access publication & EERA JP Certificate):

Tabea Stadler from KIT-IMVT, with her presentation "Syngas Production in the KEROGREEN Process Chain: Development of a compact Sorption-Enhanced Water-Gas Shift Reactor."

More Information…

KEROGREEN: https://www.kerogreen.eu/

BECCU: https://www.beccu.fi/

E-Fuel: https://www.e-fuel.fi/

EERA JP Energy Storage: https://www.eera-energystorage.eu/

ABSTRACTS of presentations*

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*in alphabetic order

Author: Manuel Andresh[1]

Title: Quantitative model-based assessment of global socio-ecological challenges and opportunities for the transition to Power-to-X: Case study for the aviation sector

Abstract:

Power-to-X (PtX) is currently discussed as a chance to defossilize the transport sector and reduce its impact on the climate with synthetic fuels. The potential social and ecological impacts other than the Global Warming Potential (GWP) are rarely addressed in this context. This work is aiming at identifying the social and ecological challenges and opportunities that could arise with a transition to PtX. Aspects of dynamic and consequential Life Cycle Assessment (LCA) and Social-LCA (S-LCA) are integrated into the here developed approach. The underlying idea is that the transition to alternative fuels for a reduction in CO_2 emissions should at least not worsen sustainability aspects within other important areas. Fossil and bio-based jet fuels are integrated as benchmarks with the Sustainable Development Goals (SDGs) as normative framework. The SDGs are globally accepted and cover the most important aspects of sustainability around the world. Every SDG is connected to at least one indicator of the S-LCA or LCA or additional values and then addressed individually within this approach. It is not assumed that the production of fuels can in any way reach the SDGs by themselves, however they can have negative and positive impacts on them. The risks and potential impacts are analysed on a global scale with modelled PtX constellations for each country / region with country-specific conditions for wind and photovoltaic power. It is assessed how many of the PtX constellations can reach the fossil and bio-based benchmarks and which SDGs are affected the most (positively and negatively). Additionally, a 2050 scenario is integrated to account for potential changes in technologies and costs. The structure of the model and first preliminary results will be presented.

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[1] PhD Day presentation

Author: Aki Braunschweiler[2]
Title: Light olefin production from CO_2

Abstract:

The light olefin production from CO_2 happens through two consecutive reactions: reverse water gas shift (RWGS) and Fischer-Tropsch (FT), where the FT reaction is catalyzed with iron catalyst suitable for high temperature Fischer-Tropsch (HTFT) that is capable of producing light olefins with a good selectivity. In the BECCU project, the production of light olefins from CO_2 was studied in a laboratory scale RWGS+FT setup with different FT catalysts and process conditions were tested. The tested catalysts were Fe-Mn/Al_2O_3 and Fe-Na-S/Al_2O_3. The catalysts were tested at different temperatures, with different space velocities (residence times) and different H_2/CO ratios. The best light olefin selectivity was obtained with Fe-Mn/Al_2O_3 catalyst with gas hourly space velocity of 4250 h^{-1} and H_2/CO ratio of 1, where the selectivity was between 48.6 % and 52.3 %. depending on temperature. The recycling of product gases was also tested with washcoated Fe/Al_2O_3 catalyst. The recycling of product gases improved the light olefin selectivity up to 63.7% as well as the overall conversion

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[2] PhD Day presentation

This project has received funding from the European Union's Horizon 2020
Research and Innovation Programme under grant agreement No 763909.

Authors: **Dorela Dhamo**, Jannis Kühn, Michael Rubin, Roland Dittmeyer
Title: Defossilizing the aviation sector with synthetic fuels

Abstract:

One of the biggest challenges of the 21st century is the anthropogenic climate change. According to bp Statistical Review of World Energy around 34 thousand million tons of CO_2 were emitted in 2019, an increase of approximately 0.5 % worldwide. The transport sector is responsible for up to 24 % of these CO_2 emissions.

Beside other alternatives to defossilize the transport sector like electro mobility and fuel cells – technologies that might be implemented in the road traffic – in the long distance transport, renewable synthetic fuels play an important role in the early replacement of the current used fuels. The existing filling-station network, the current infrastructure and engines can continue to be used.

The synthesis of these renewable synthetic fuels starts with the separation of CO_2 from the air. Other carbon sources like biomass are also possible. After the CO_2 capture, synthesis gas preparation via e.g. electrolysis takes place. Synthesis gas serves as an educt for the next step, Fischer-Tropsch synthesis, where hydrocarbon chains different length und type are produced. These Fischer-Tropsch products do not meet the requirements of the current fuels and therefore, need to be upgraded in further steps. Depending on the hydrocarbon's length/type, and the target final molecule, several upgrading steps take place, like hydrocracking, isomerization, hydrotreating etc. The whole process is known as the Power-to-Liquid route.

This work focuses on branched molecules with a high octane number, such as isooctane, which is a very important component of gasoline and aviation gasoline. The concept of a possible Power-to-Liquid route for the production of these molecules and the effects of the process conditions on the Fischer-Tropsch product distribution have been investigated and will be presented in the poster. Preliminary design of the further experiments comprising the isomerization step and its coupling with the Fischer-Tropsch synthesis will be described.

Authors: **Emil Drazevic**, Jacopo Catalano, Michalis Tsampas, Stefan Welzel, Adelbert Goede, Saso Gyergyek, Anja Sedminek, Luka Skubic, Vesna Middelkoop, Marijke Jacobs, Farnaz Sotoodeh, Vivek Sinha, Alberto Garbujo, Jun Maruyama, Zyun Siroma

Title: Decentralized production of green and sustainable ammonia – insights from EU/Japan collaboration

Abstract:

Renewable energy sources are considered a main solution to decarbonize the power sector. However, the production of electrical energy from renewables is rarely matched by consumption. Ideally, the renewable electrical energy should be stored when the wind is not blowing and the sun is not shining. Storing excess electrical energy in chemical bonds appears as an obvious choice for long-term energy storage. Electrical energy could be stored in H_2 using an electrolyser and later use H_2 as a fuel; however H_2 has low volumetric energy density and is difficult to transport. Ammonia on the other hand (NH_3) appears as a good candidate for the long-term storage because it has a much higher volumetric energy density and it is much easier to transport and can be cracked either to produce H_2 or used as a fertilizer. Today almost all ammonia is produced by the Haber-Bosch process, which can be completely electrified using off-the-shelf technologies. Haber-Bosch, however, is heavily centralized. Renewable energy from sun and wind, on the other hand, are decentralised and diluted. Therefore, the search is for an alternative to the conventional Haber-Bosch process, relevant for smaller, decentralized scales directly coupled to the renewable energy sources. In the ORACLE project we look into three different pathways to produce sustainable ammonia: i) electrified Haber-Bosch reactor to serve as a benchmark; ii) Electrochemical synthesis of NH_3 and iii) plasma-assisted electrochemical synthesis of ammonia. This talk introduces the main advantages and challenges associated with these processes.

Author: Joachim Falkenhagen
Title: “Green Future Quota” for power-to-X fuels like green hydrogen and kerosene

Abstract:

Political instruments to support renewable energy development include carbon taxes, government grants for investment, support for production in the form of feed-in tariffs or CfD, and quota obligations. The existing level of carbon taxes or prices in the EU ETS are insufficient to support high-cost measures like the substitution of fossil fuels with power-to-X fuel. Carbon pricing gets opposition because significant transfers to the state take place, while the incentive shall support efforts where ultimately no or less carbon dues will be paid. With a zero Carbon future in mind, the political will to set up and reinforce a scheme, which shall become obsolete soon, appears limited.

Feed-in-tariffs for renewable energy have gained traction for some while. They lead to investment in renewables quickly, while spreading the costs over future decades. Their acceptance has waned when the cumulative cost effect became more apparent.

Quota systems are widespread in the regulated, monopolistic US power utilities (renewable portfolio obligations). In competitive power markets, providers for the fulfilment of quotas must fear an abolishment of quotas, and new market entrants with cheaper technology.

A quota shall usually lead to an increasing share of renewables in the energy mix, so that fulfilment costs increase over time.

The consumption of fossil fuels should be weighted with additional dues in line with the climate damage made, so that consumers avoid fuel-intensive products and services and providers strive for a less fuel-intensive production. These levies would start rather high and then recess with decarbonization.

This conflict can be solved with power-to-X quotas where the obligation can be fulfilled over an extended time, e.g. 10 or 20 years after emissions. The quota fulfilment from several base years will cumulate over time. The scheme also allows for low-cost financing of the investments required to fulfil the quota.

Further details of the proposition are addressed.

Author: Christian Frilund
Title: CO_2 conversion to hydrocarbons using reverse water gas shift and FT-synthesis

Abstract:

The E-FUEL concept is based on Power-to-X (PtX) production models, in which renewable electricity will be converted into hydrogen by high temperature electrolysis and combined with flue gas captured CO_2 to produce synthesis gas. This syngas will be converted to paraffinic transportation fuels through Fischer-Tropsch (FT) and upgrading steps. To produce these species, VTT is employing a thermocatalytic reverse water-gas shift (rWGS)/Catalytic partial oxidation (CPOx) reactor and coupling it to the FT. An E-FUEL PtX demonstration plant located at an industrial site is planned for 2023.

The thermodynamics dictates that the rWGS reaction, which is endothermic, is favoured at high temperatures. As the downstream FT synthesis is operated at 15 - 30 bar pressure, it is practical to also pressurize the rWGS reactor. However, at higher pressures more methane is formed, which has an impact on the overall efficiency of the process. This again favors choosing a high operation temperature of 800–900 °C. The rWGS/CPOx process enables utilization of FT outlet gases, consisting of unreacted species and light FT hydrocarbons. Oxygen provides the heat to the reactions, allowing for autothermal operation. It is also vital in the control of solid carbon formation, one of the major practical issues of rWGS systems, which further increases in the presence of FT hydrocarbons. The coupled rWGS/CPOx-FT system increases the CO_2 efficiency from 50-60% to 80-90% compared to a once-through setup.

The focus of this presentation is in the experiences with a fully integrated CPOx/rWGS-FT process, which has been constructed for VTT's Mobile Synthesis Unit (MOBSU). Technical validation and feasibility of the system is assessed.

This project has received funding from the European Union's Horizon 2020
Research and Innovation Programme under grant agreement No 763909.

Authors: **V. Gil,** K. Tadanaga, H. Gröger, S. Wuttke, J. Gurauskis, P. Camargo, R. Guidici, F. Bonino, J. Hadermann, C. Rosero, M. Aparicio, R. Fernández

Title: Air Carbon Recycling for Aviation Fuel Technology

Abstract:

A recent Horizon 2020 funded project (Air Carbon Recycling for Aviation Fuel Technology, 4AirCRAFT) in International cooperation with Japan for Research and Innovation on alternative renewable fuels will be presented.

4AirCRAFT's ultimate goal is to develop a next generation of stable and selective hybrid catalysts for the direct CO_2 and H_2 conversion into C_8-C_{16} (jet fuels for aviation sector). 4AirCRAFT will overcome the current challenges by combining three main reactions into one cascade reactor to increase the CO_2 conversion rate and simplifying the process. By achieving this we will be able to circumvent the need for further steps for hydrocracking or hydrorefining of Fischer–Tropsch waxes.

The novel technology will produce sustainable jet fuel at mild conditions, reducing energy consumption and contributing to a circular economy, leading to a decrease in greenhouse gases emissions and reduced dependence on fossil fuel-based resources.

In summary, 4AirCRAFT combines hybrid catalytic conversion and process intensification to bring out an efficient, precise, flexible and scalable unique technology to direct convert recycled CO_2 into sustainable and clean liquid fuels, thus making flying carbon neutral.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 101022633. This work is supported by Japan Science and Technology Agency (JST) under Grant Agreement No JPMJSC2102. This project is developed in the frame of a Mission Innovation Challenge.

Authors: **Mery Hernandez**, Alexander Navarrete, Roland Dittmeyer

Title: Plasma assisted H_2O_2 synthesis from water and oxygen

Abstract:

Hydrogen Peroxide (H_2O_2) is considered the preferred green chemical for many industrial processes given that water is the only H_2O_2 degradation product. Since the common H_2O_2 synthesis process (Anthraquinone Auto-Oxidation) is not environmentally friendly, many alternatives have been proposed. One of them is the direct synthesis from H_2 and O_2 in the presence of a catalyst. Nevertheless, effective catalysts for this reaction usually involve noble metals deployment, affecting the sustainability of such process.

Plasmas are an alternative platform for a decentralized H_2O_2 production that do not require noble metals, have instant on/off time, and can activate molecules such as oxygen and water. Promising results have been reported for discharge and gliding arc plasma reactors regarding yield and selectivity to H_2O_2. Microwave plasmas are not usually studied in this process, but they are very interesting since they can handle higher gas flow rates, do not require electrodes and have shown potential for efficient use of energy in comparison with the other plasmas. Nevertheless, the direct combination of H_2 and O_2 at high temperatures usually present in microwave plasmas (up to 3000K) are a concern for safety reasons.

In this sense, in line with decentralized concepts, it is proposed to directly use water in combination with oxygen to produce H_2O_2. The interface between water and plasma would be the main study object, along with the mixing regime, spray conditions and flow pulses which have shown to affect both the efficiency and yield of the reaction, balancing the increased contact of plasmas and water together with the reaction control inside the aqueous phase. When plasma is in contact with water, the plasma-water interactions can lead to many direct reactions at the plasma-water interface and indirect side reactions in the bulk water.

Authors: **Peter Holtappels**, David Tran

Title: Organic Electrosynthesis: a sustainable route to polymers and other high value chemicals?

Abstract:

In advancing towards a more sustainable society, biomass and (electro)catalysis will play a leading role in the development of green chemistry and in the generation of renewable chemicals and fuels. To date, oil and natural gas are the main feedstock for producing the commodity chemicals that everything from medicine to paint is based on today. In a future sustainable chemical industry, the use of natural gas as energy, hydrogen, and carbon source must be replaced by renewable electricity, water, biomass and/or CO_2, respectively.

Organic electrosynthesis, which often involves hydrogenation and oxidation reactions, can be a key technology to electrify the chemical industry and produce valuable organic compounds in a more green and sustainable manner from water and biomass derived compounds. The contribution will briefly introduce the concepts of organic electrosynthesis and its previous application in the synthesis of organic compounds. A novel type of reaction is to synthesize commodity chemicals such as Ethylene Glycole (EG) for the synthesis of polymers and plastics such as polyethylene terephthalate (PET), a biobased polymer. Advanced concepts for the electrochemical cells such as Tandem Electrochemical Reactors and Flow reactors, which aim to intensify the synthesis process in terms of energy efficiency and selectivity, will be explained and actual research attempts introduced. First results related to the search of suitable electrocatalysts for the desired synthesis reactions will be presented.

Authors: **Marijke Jacobs**, Leif Olav Jøsang and Vesna Middelkoop

Title: Development of thin electrode layers by spray coating for solid oxide cells

Abstract:

This study investigates the innovative use of a deposition technique, spray coating, for the fabrication of optimal thicknesses of solid oxide cell (SOC) layers on a range of SOC-compatible materials. The work has been carried out as part of the European KEROGREEN project that aims to utilize CO_2 into sustainable aircraft kerosene. To separate the oxygen at higher operating temperatures after CO_2 dissociation (plasmolysis) for creating a CO stream for Fischer-Tropsch downstream synthesis, a solid oxide electrolyzer cell is used. For the electrodes, the most promising LaSr-based perovskite materials were selected based on their electrical conductivity and ability to suppress the CO to CO_2 back reaction at the CO_2 (plasma) splitting side. The coating parameters such as atomization pressure and coating speed were optimized to obtain uniform coatings and to control the thickness. The suspension formulation was adjusted to improve the adhesion and the quality of the coating. Profilometry and microscopy were used to determine the coating thickness and porosity. Furthermore, electrochemical impedance spectroscopy were carried out.

Several YSZ discs were first coated with a dense interlayer to prevent reactions between electrolyte end electrodes. Then, an oxygen and plasma electrode layer were applied, followed by thermal treatment up to 1100 °C for 2h. The coatings show a good adhesion to the YSZ discs and look rather uniform. Both electrode layers are porous and are about 10 µm thick, while both interlayers are dense and only of a few µm thickness. The total electrodes impedance determined at 800 °C in dry air was reduced by using the extra interlayer to prevent interactions compared to the impedance of the cell without interlayers. The LaSr-based electrode powder and spray coated SOEC remained stable in the CO_2/CO/O_2 environment.

This project has received funding from the European Union‘s Horizon 2020 Research and Innovation Programme under grant agreement No 763909.

Author: Vafa Järnefelt
Title: The potential of CCU technologies in mitigating climate change

Abstract:

Carbon capture and use (CCU) technologies have an enormous potential in reducing environmental impacts and mitigating the climate change, however applied alone, these technologies do not have the capacity to solve the climate crisis. From a climate change mitigation perspective, avoiding current emissions should be a priority, while simultaneously directing focus on developing solutions to current challenges for which CCU and CCS technologies and their combination can be a tangible solution alongside other technologies.

The beneficial effects of the CCU technologies from the environmental aspect are highly dependable on set of variables, as well as time and space. The carbon storage varies significantly between different CCU technologies, where the storage time can range from a day to thousands of years. The net climate impact of a CCU solution also depends to a large extent on the emission intensity of the applicable processes.

Mitigation measures require long-term storage of carbon dioxide, at least for centuries or thousands of years. Thus, the so called fast ‘cycling’ applications of the CO_2 do not create the needed impact for mitigating the climate change but enable reducing or completely avoiding the use of fossil resources, which would otherwise end up as emissions to atmosphere. Furthermore, adoption of CCU technologies can lead to reduction of overall production emissions, i.e., positive effects can be achieved beside the CO_2 reduction also in other environmental impact categories such as reduced acidification and eutrophication.

Authors: **Jan-Willem Könemann**, Maartje Feenstra

Title: Take-Off a novel process to synthetic aviation fuel

Abstract:

Aviation is one of the most challenging sectors when it comes to reducing CO_2 emissions. Conventional sustainable alternatives, such as electrification or hydrogen propulsion, are not expected to be suitable substitutes for long-haul flights in the coming decades. Sustainable aviation fuel (SAF) made from biogenic or synthetic origin can make sustainable aviation possible. Biogenic SAF is still the most economical alternative. Synthetic SAF will play an important role in the future as it is has an unlimited feedstock.

The EU project 'Take-Off: Production of synthetic renewable aviation fuel from CO_2 and H_2', launched in January 2021, will, over the next 4 years, provide a detailed picture of the technical, environmental and economic performance of a novel route to synthetic SAF. This technology route aims to deliver a highly innovative process that produces SAF from captured CO_2 via light olefins as intermediate. The result is a more selective process that produces SAF at considerable lower cost and higher energy efficiency compared to other power-to-liquid alternatives.

Author: Mikko Lappalainen
Title: State-of-the-art and future mapping of electrolyser technologies

Abstract:

Hydrogen production by water electrolysis is currently getting considerable attention. Electrolysis technologies are developing and becoming more feasible to produce hydrogen from green electricity. System capacities are increasing and specific investment costs are decreasing. The state-of-the-art and future mapping presents the key parameters and future development of today's most common commercial electrolyser technologies, alkaline and PEM electrolysis. In addition, strategies, plans and actions to build large-scale electrolyser projects are discussed.

Authors: **Onni Linjala**, Tuula Kajolinna

Title: CO_2 supply options for P2X and results from carbon capture experiments

Abstract:

Carbon capture is an essential technology for Power-to-X value chains that require a supply of carbon. There are several industrial emission point sources that could be potentially harnessed to provide CO_2 for utilization. Many types of technologies, such as liquid absorbents, solid sorbents, and membranes, have been developed to extract and capture CO_2 from various gas streams. As the different emission streams and capture technologies have unique characteristics, implementation of carbon capture into an industrial process is a case-by-case matter that requires evaluating characteristics of the emission stream, technical requirements of the applicable capture technologies and the desired capture performance (i.e., CO_2 purity, capture efficiency and capture cost).
Various industrial emission streams and capture technologies have been evaluated in BECCU and E-Fuel projects to identify CO_2 supply options with high techno-economic potential in CCU/P2X routes. Furthermore, the projects include testing of carbon capture with different technologies at industrially relevant conditions for concept validation and technology development.

This project has received funding from the European Union‘s Horizon 2020
Research and Innovation Programme under grant agreement No 763909.

Author: Miia Nevander

Title: Techno-economics of the synthesis route from CO_2 and clean H_2 to polycarbonate polyols (BECCU)

Abstract:

Carbon dioxide usage to produce high-performance polymers, such as polycarbonate polyols, has accelerated in recent years. However, only a maximum of 50% of the carbon in the product originates from CO_2, while the rest comes from fossil sources. In BECCU project, VTT together with project partners develops a novel concept to produce polycarbonate polyols, where up to 100% of carbon is originating from carbon dioxide. The process utilizes biogenic CO_2 and clean hydrogen to produce polyols via catalytic partial oxidation, Fischer-Tropsch, epoxidation and polymerization syntheses.

Techno-economics of the BECCU process have been preliminarily evaluated, and the results look promising. As the calculated production costs are low compared to the anticipated selling price, the production of these specialty chemicals appears attractive. The production cost of polyols was found most sensitive to the cost of electricity needed in electrolysis and the capital investment annuity.

This project has received funding from the European Union‘s Horizon 2020
Research and Innovation Programme under grant agreement No 763909.

Authors: **Sari Rautiainen**, Juha Lehtonen

Title: Fossil-free polycarbonate polyols from captured carbon dioxide and renewable hydrogen

Abstract:

Carbon dioxide has recently been used as feedstock to produce high-quality polymers, such as flexible polyurethane foams. So far, only approximately 20 % of the feedstock has been CO_2 while the rest is fossil-based epoxides. Due to large market volumes of these polymers, millions of tons of CO_2 could be utilized annually on a global scale. VTT is developing a concept where polycarbonate polyols are produced from CO_2 and renewable power. CO_2 captured from industrial sources, hydrogen obtained from water electrolysis or as a by-product from the industry are converted into olefinic hydrocarbons in a two-step process. First carbon monoxide is produced by a combination of reverse water-gas shift (rWGS) reaction and catalytic partial oxidation (CPOX). Then carbon monoxide and hydrogen are converted to hydrocarbons by Fischer-Tropsch synthesis using a proprietary Fe-based catalyst leading to a high yield (> 45 %) of light olefins. The produced light olefins (C2-C4) are further oxidized into epoxides using hydrogen peroxide and the obtained mixture of epoxides is co-polymerized with CO_2 and a starter polyol into polycarbonate polyols to applied for polyurethanes. Our presentation focuses on the experimental work of mixed C2-C4 olefins epoxidation and subsequent mixed C2-C4 epoxides copolymerization with CO_2 to polycarbonate polyols.

Authors: **Esperanza Ruiz**, José María Sánchez

Title: Process intensification for advancing Power-to-Fuels

Abstract:

One of the main challenges for advancing the conversion of renewable energy and CO_2 to fuels (Power-to-Fuels), via CO_2 adsorption and catalytic hydrogenation, is increasing the energy efficiency of the process and reducing the costs (CAPEX and OPEX). The tendency is to maximize the CO_2 uptake and the yield to the desired product with a minimum energy input.

In general, these processes are favoured at high pressures (high compression power) and low temperatures and are slow processes, requiring high residence times (high reactor volume), feed recycling ratios or cyclic operation (high power consumption). In addition, the presence of water may cause inhibition and hydro-thermal deactivation (lower lifetime).

An option to face these challenges is through process intensification, developing integrated systems which combine various processes in a more efficient single step that allow, for example, the selective activation of the adsorbent/catalyst by electrochemical means and in-situ generation of the H_2 necessary for the reaction, by water electrolysis (or other H+ producing reaction), in single and double chamber solid oxide electrolyte cells, respectively, operating at atmospheric pressure. Another alternative is the use of some innovative configurations, such as sorption enhanced catalytic reactors, for shifting the CO_2 hydrogenation equilibrium via in situ water adsorption, or cyclic reactive adsorption processes, using hybrid (water selective sorbent and catalyst active for CO_2 hydrogenation), dual function materials for coupling the endothermic CO_2 desorption step, with renewable H_2, with the exothermic CO_2 hydrogenation in a single isothermal atmospheric reactor, or multicatalytic materials combining active phases for different step reactions (e.g. RWGS/CO-Fischer Tropsch/hydro-isomerization).

This work reviews different innovative alternatives proposed to improve CO_2 adsorption and catalytic hydrogenation to fuels and presents CIEMAT research on these technologies.

Author: Ville Saarinen
Title: High temperature electrolysis and co-electrolysis for production of green hydrogen and syngas

Abstract:

High temperature Solid Oxide Cell (SOEC) technology enables electricity conversion into hydrogen with high Power-To-Gas (AC to H_2) efficiency (80-90%). SOEC technology is reversible: the same system can work both as a fuel cell and an electrolyser depending on power generation and grid stabilisation needs. Physical structure of SOEC stack consists of cells packed together and the total capacity depends on the number of cells. Also, SOEC has capability for co-electrolysis of steam and CO_2, which enables more efficient power-to-X, if integrating them as part of industrial processes. This presentation describes implementation of movable "10-foot container" size SOEC system in a 10 kW pilot demonstration scale, where special attention is paid to heat integration: heat losses are minimized with optimized Balance of plant (BoP) component design, placement and insulation. The developed system is highly instrumented enabling detailed system analysis, e.g. the calculation of enthalpy flows and efficiencies of all BoP components.

This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under grant agreement No 763909.

Authors: **Georgios Sakas**, Alejandro Ibanez-Rioja, Vesa Ruuskanen, Antti Kosonen, Jero Ahola, Olli Bergmann[3]

Title: Dynamic energy and mass balance model for an industrial alkaline water electrolyzer plant process

Abstract:

The presentation demonstrates a parameter adjustable dynamic mass and energy balance simulation model for a 3 MW and 16 bar industrial water electrolyzer plant process. The aim of the process simulation is to enable future optimization studies on the cost and energy efficiency of the plant. Verification of the electrochemical and thermal models was achieved using measurements from an analogous real industrial plant of the same power and pressure range having the same operating system designs. The results show that at steady-state and nominal power operation, the shunt currents were the main contributor of relatively low Faraday efficiency of 86 %, and heat loss to ambient from the stack was just 2.6 % of the total power loss. In addition, a Sankeys diagram of the power distribution in the stack and system level is demonstrated, which was based on steady-state studies of the simulation process.

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[3] PhD Day presentation

This project has received funding from the European Union‘s Horizon 2020 Research and Innovation Programme under grant agreement No 763909.

Authors: **Tabea J. Stadler**, Peter Pfeifer[4]

Title: Syngas Production in the Kerogreen Process Chain: Development of a compact Sorption-Enhanced Water-Gas Shift Reactor

Abstract:

In the KEROGREEN project, an unconventional PtX route will be tested in a pilot scale plant. The crucial step of CO_2 activation is realized by means of CO_2 plasma splitting into CO and O_2. The purified CO is then partly converted with steam to produce hydrogen. In this process step, two main targets are pursued in a so-called sorption-enhanced water-gas shift reactor (SEWGS): 1) providing syngas with a H_2/CO ratio of approximately two for the subsequent Fischer-Tropsch synthesis (FTS); 2) removing the by-product CO_2 and refeeding it to the plasmolysis unit.

In the FTS reactor, hydrocarbons with a wide chain-length distribution are formed. The kerosene yield can be increased in the hydrocracking unit, where long-chained hydrocarbons are cracked down to the kerosene range (approximately C10-C14).

In this contribution, the following aspects regarding the development of the compact SEWGS reactor system for continuous syngas production in the KEROGREEN project will be addressed:

1) Choice of materials and process conditions resulting from lab-scale experiments
2) SEWGS reactor design and module integration in the KEROGREEN pilot plant
3) Modeling concepts and results in Matlab/Simulink for dynamic process operation
4) Investigation of the influence of SEWGS performance on subsequent process steps

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[4] PhD Day presentation

Authors: **Marjut Suomalainen**, Miia Nevander, Markus Hurskainen, Jari Pennanen

Title: Techno-economic assessment of producing diesel from CO_2 and H_2O via co-electrolysis and Fischer Tropsch synthesis

Abstract:

The techno-economic assessment was performed for diesel produced via Fischer Tropsch synthesis and using co-electrolysis for syngas production. The assessment included CO_2 capture and purification unit based on amine-based absorption (MEA), conversion of CO_2 and water to syngas in the solid oxide electrolyser (SOEC), Fischer Tropsch synthesis, and fractionation and refining of the synthesis products to diesel and by-products. Flue gas from power plants and process heat generation was considered as the source of CO_2. Capacity for the assessment was defined by flue gas input of 315 t/h, of which 20 wt% was CO_2. Mass and energy balances were calculated using Aspen Plus steady state process modelling software and a spreadsheet software MS excel, and the parameters for mass and energy balances were based on VTT's in-house data, data from project partners or data available from literature. Preliminary result included the electrical efficiency to liquid fuels (diesel and gasoline) 48% with used assumptions. Thus, for 500 000t/a CO_2 converted to 63 000 t/a diesel and 50 000 t/a gasoline, the electricity demand was 310 MW. Operation of SOEC consumed 91% of total electricity demand. Based on pinch analysis, maximum district heat potential was 55 MW (120-70 °C), when applying heat pump for low-grade heat. Estimated CAPEX of the plant was 550 M€, of which 41% consisted of SOEC. Production cost for liquid fuels with used assumptions ranged from 1000-1700 €/t when electricity price ranged from 20-50 €/MWh. The electricity cost and the annualised investment cost were the most significant cost factors. Sensitivity analysis confirmed the importance of the electricity price to the production price of the liquid biofuels (diesel, gasoline).

Authors: **M.N. Tsampas,** R. Sharma, S. Welzel, M.C.M. van de Sanden

Title: Synergistic combination of plasma and electrocatalysis for nitrogen fixation by water

Abstract:

Thermal catalysis has a central role in chemical industries, however due to the carbon dioxide emissions caused by the combustion of fossil fuels involved in such processes the electrification of these chemical transformations is a necessary response to climate change. Plasma catalysis and electrocatalysis have attracted high interest due to their potential to drive sustainable chemical processes.

Plasma catalysis can activate and selectively transform a variety of stable molecules to desired products. High energy electrons generated in plasmas can excite ground state gas-phase molecules, allowing them to react on catalytic materials at milder conditions than possible thermally. In electrocatalysis electrons are exchanged between electrodes/electrocatalysts and reactants to modify the rate of electrochemical reactions by altering the reaction pathways and decreasing the activation barriers.

In this contribution we will present an innovative combination of the two fields for the case of nitrogen fixation by water. We employ electrochemical systems with proton or oxygen ion conducting membranes for providing reacting species on electrocatalysts while RF plasmas are used to increase the reactivity of nitrogen. The spatial separation of nitrogen activation and water dissociation provides true independent parameters for performance optimization. Concentration of products is orders of magnitude higher than equilibrium and high selectivities towards desired products are observed.

Authors: **S. Welzel**, F.J.J. Peeters, W. Bongers, M.C.M. van de Sanden, M. Tsampas

Title: CO_2 plasmolysis in the KEROGREEN process chain: Development of a plasma reactor module for CO production

Abstract:

The KEROGREEN process is based on an unconventional Power-to-X route. An all-electrical driven container-sized, pilot scale plant will be realised. Upstream the KEROGREEN process a plasma-based CO_2 conversion module provides the CO required in the subsequent process steps to produce the hydrogen, higher hydrocarbons and finally kerosene.

This contribution will briefly summarise the recent insights into the CO_2-to-CO conversion process by means of microwave based plasmas and elaborate further on the translation of these scientific results into engineering constraints for a container-sized plasma module. More specifically, the following topics will be discussed:

1) Plasma reactor design and preparation for integration with downstream gas separation.
2) Theoretical prediction of a suitable window of operation.
3) First experimental verification of the desired CO output.
4) (optionally) Outlook onto the remaining steps for successful match with subsequent process steps

This project has received funding from the European Union‘s Horizon 2020
Research and Innovation Programme under grant agreement No 763909.

Presentations [*]

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[*] only publishable ones, in alphabetic order

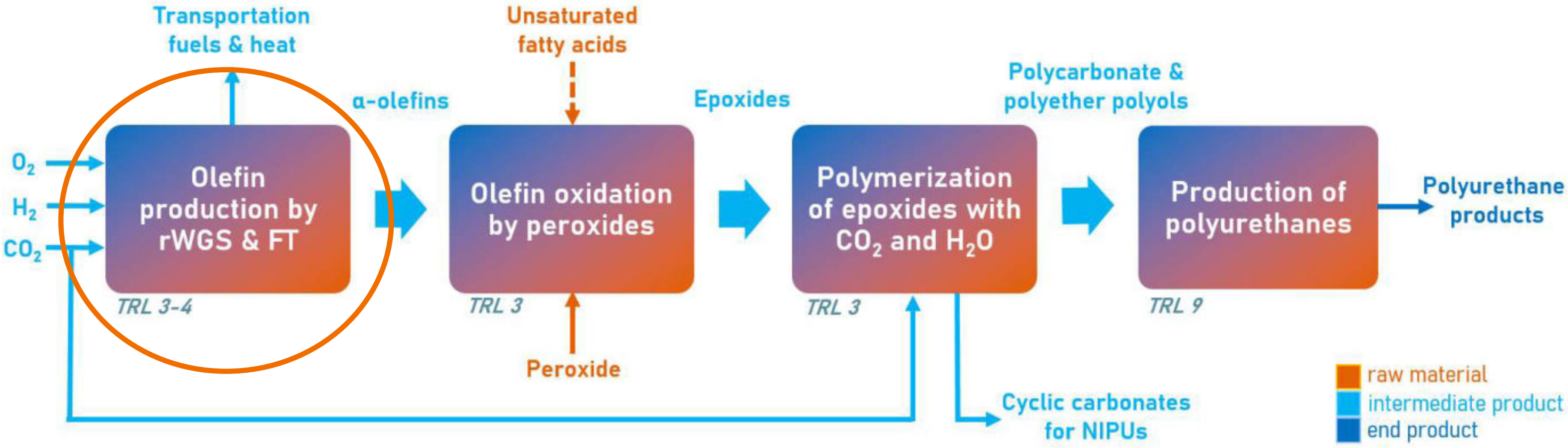
Light olefin production from CO_2

Aki Braunschweiler

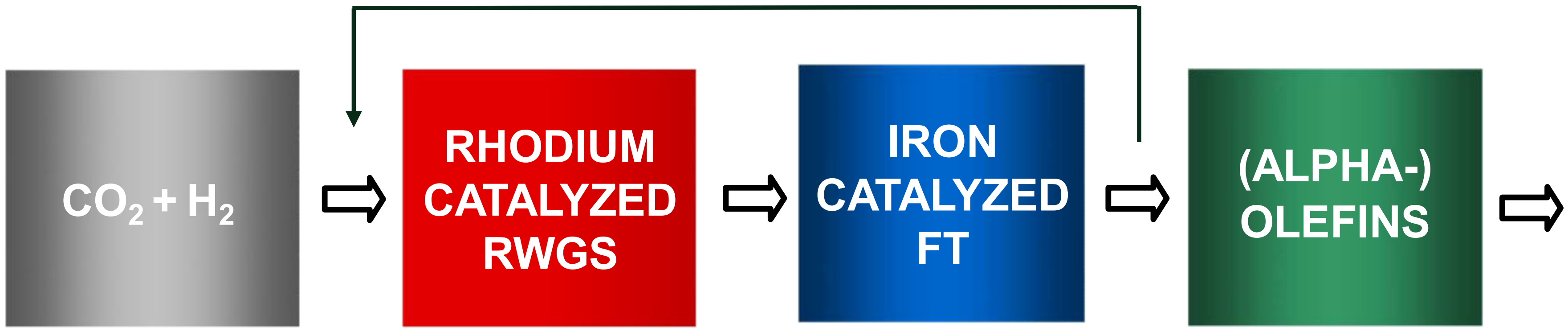
09/02/2022 VTT – beyond the obvious

Route for chemicals and polymers

- The process is based on the production of olefins through reverse water-gas shift (rWGS) and Fischer-Tropsch (FT) reaction steps.
- The yield of C2-C4 olefins is maximized to be used in polyol production and higher hydrocarbons are utilized as energy carriers (waxes or fuels)
- Potential for millions of tons of sustainable carbon usage

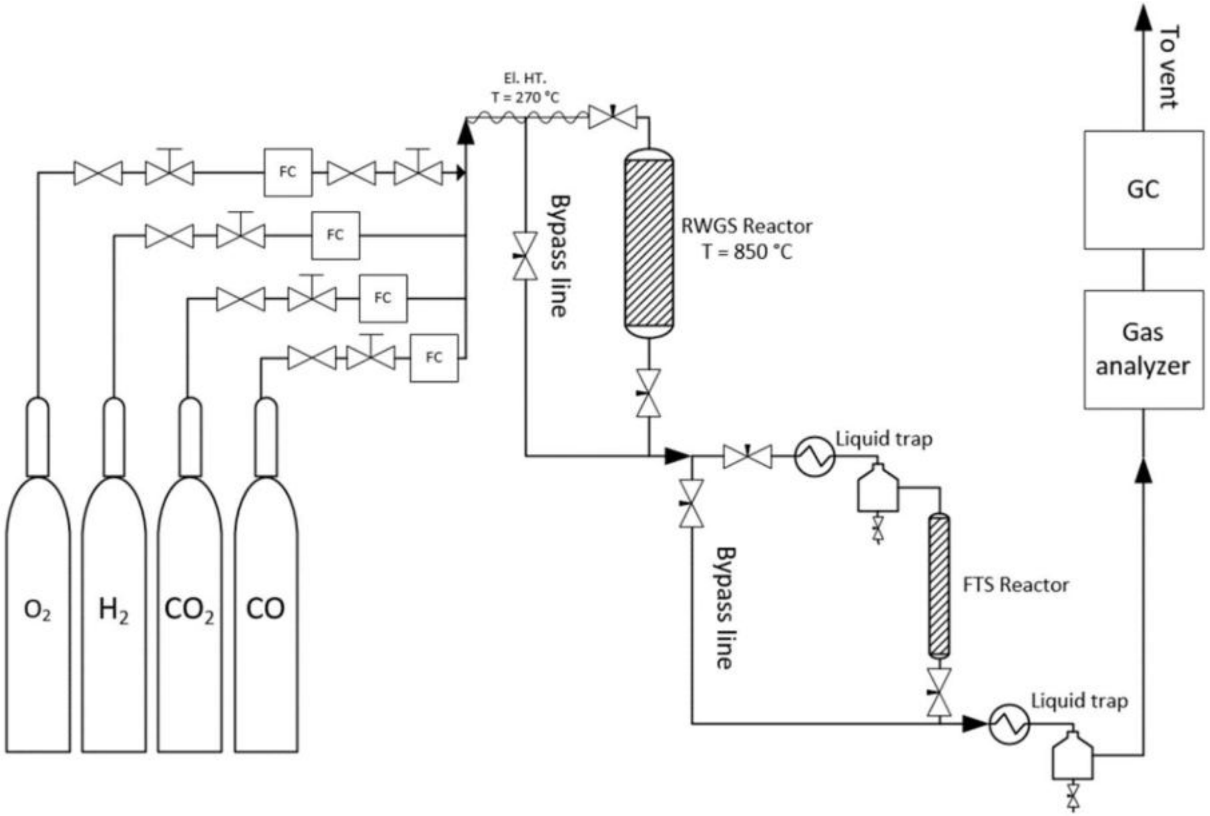


Two step process from CO_2 to light olefins



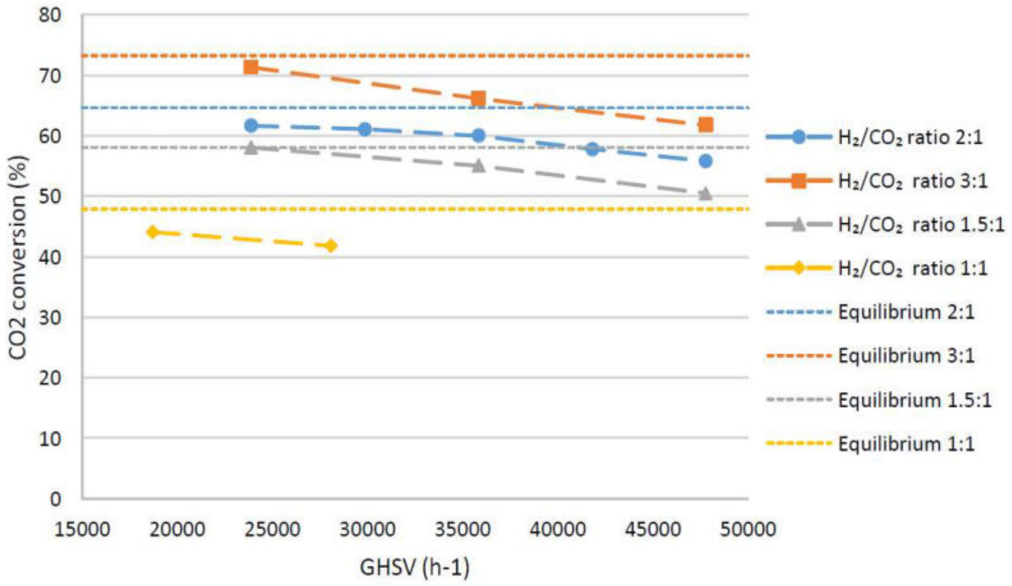
- Step 1: Reverse Water Gas Shift (RWGS)
  $CO_2 + H_2$ → Synthesis gas ($CO + H_2$) and water
- Step 2: Fischer Tropsch synthesis (FT)
  $CO + 2H_2$ → Hydrocarbons
- FT process conditions determine the quality of the hydrocarbons
- Light olefins = alkenes with two to five carbon atoms

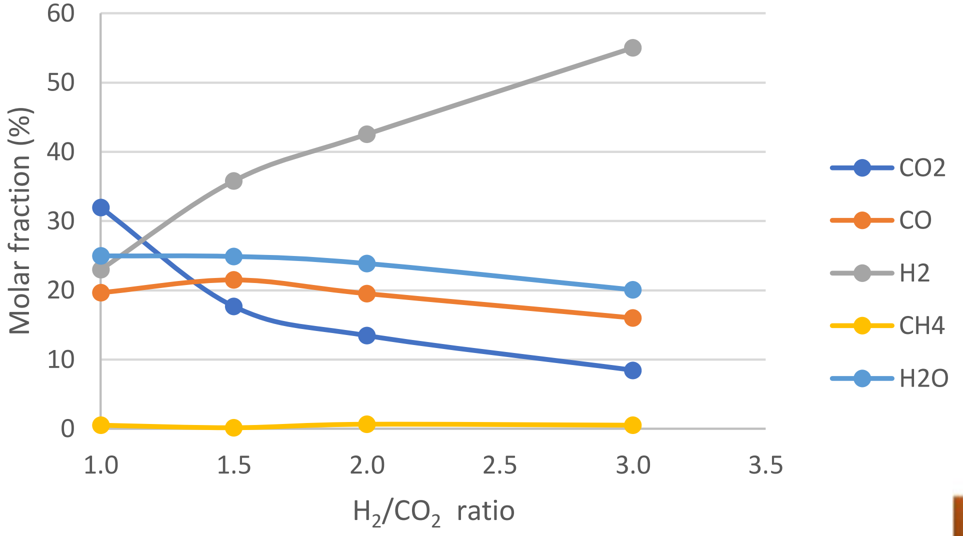
Screening for optimal process conditions



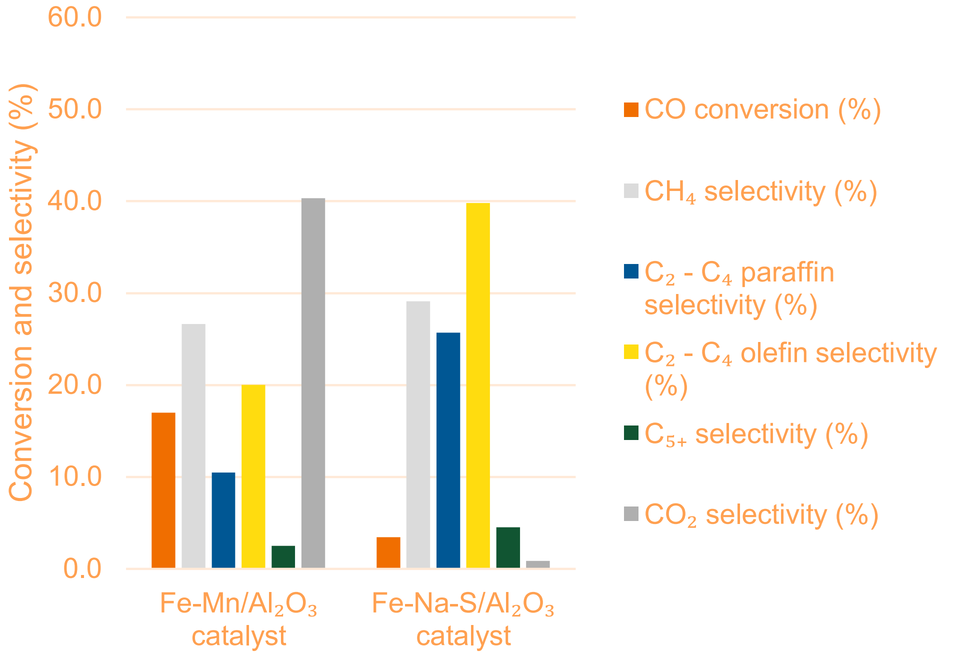
RWGS results

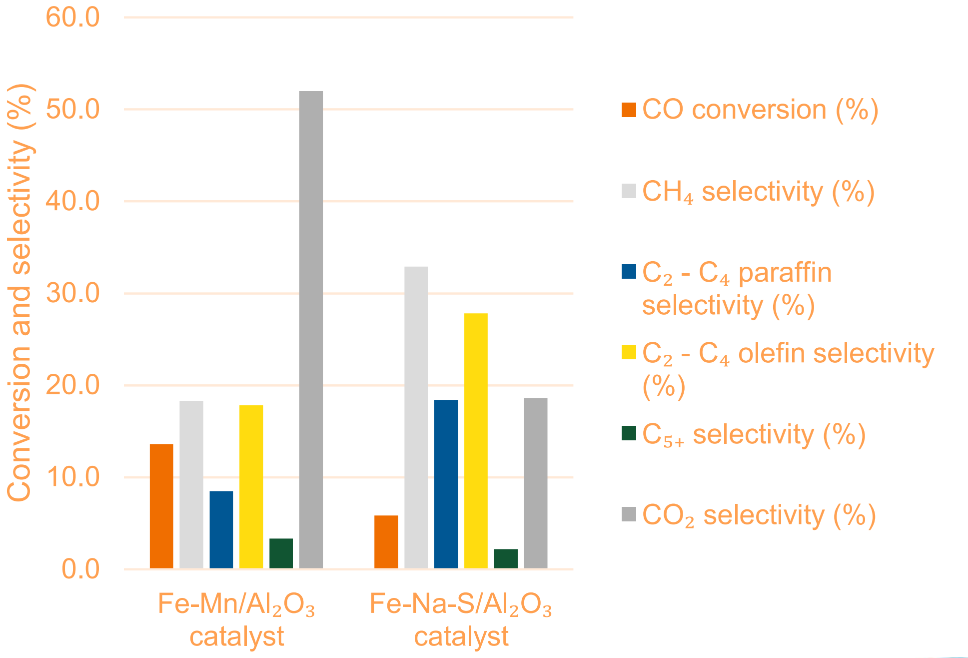
- Conversions close to equilibrium
- Good quality syngas
- Methane selectivity 2-10 %
  - Dependent on H_2/CO_2 ratio
- No catalyst deactivation
- No carbon deposition



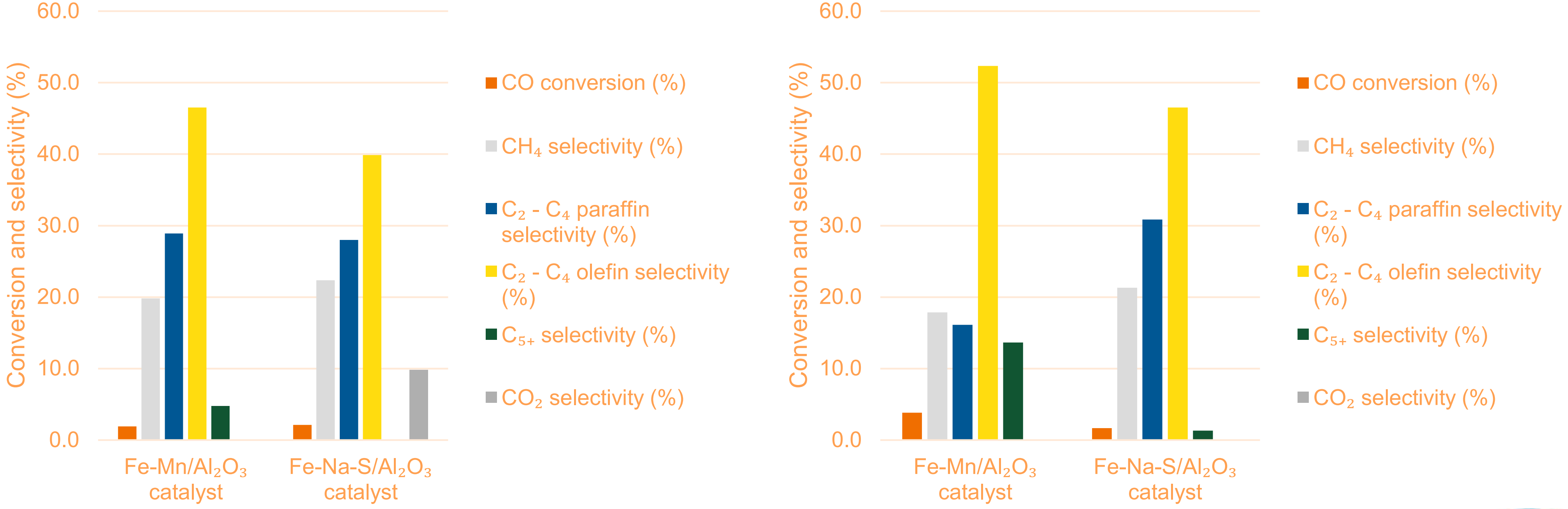


Comparison of Fe-Mn/Al_2O_3 and Fe-Na-S/Al_2O_3 at 320 °C, H_2/CO ratio of 2 and GHSV of 2200 (left) and 3400 h^{-1} (right)





Comparison of Fe-Mn/Al_2O_3 and Fe-Na-S/Al_2O_3 at 320 °C, H_2/CO ratio of 1 and GHSV of 2200 (left) and 3400 h^{-1} (right)

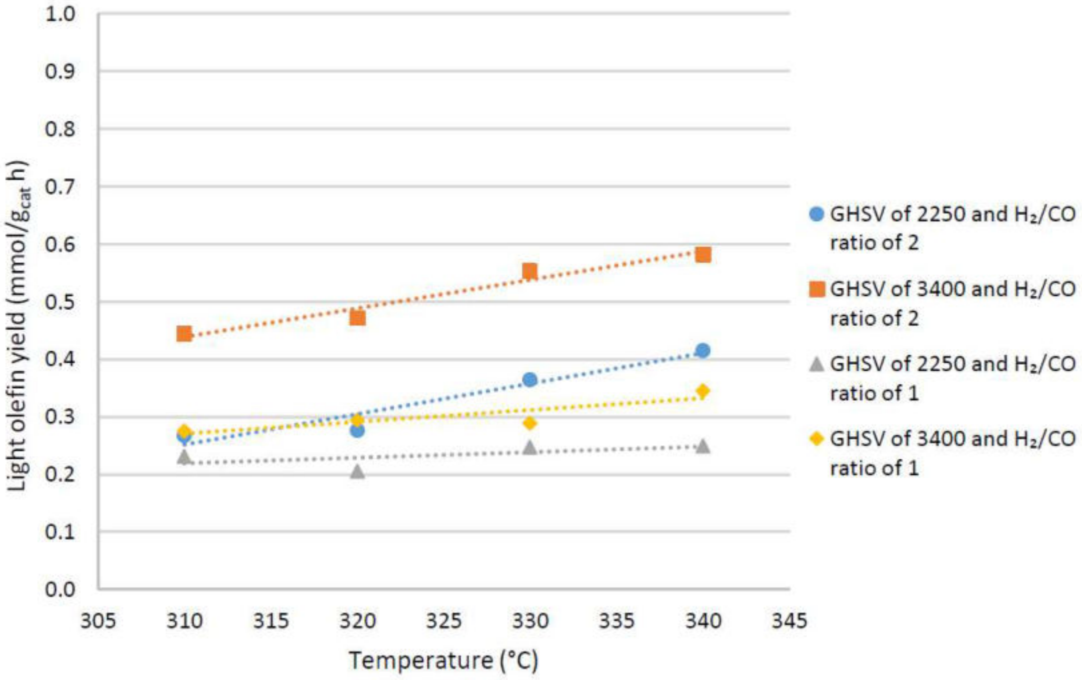


Process conditions – Olefin selectivity

- The best olefin selectivity was achieved with Fe-Mn/Al_2O_3 at 320 °C, GHSV of 4250 h^{-1}, and H_2/CO ratio of 1
  - Light olefin selectivity of 52.3 % was achieved with O/P ratio of 3
  - The selectivity ranged from 48.6 % to 52.3 % between temperatures of 310 to 340 °C
- Fe-Na-S/Al_2O_3 catalyst functioned better under different process conditions
  - Results varied between the catalysts only by a small margin
  - Although, no methane inhibition was observed, as was initially assumed to occur

Process conditions – Olefin yield

- Olefin yield increases with temperature
- Yield mostly detemined by CO conversion
  - Highest yield at conditions where the light olefin selectivity is the lowest
- Overall yield still quite low
  - Laboratory scale causes design challenges



Conclusion and future experiments

- Production of light olefins from CO_2 demonstrated for the first time at laboratory scale
- RWGS performs well, but some technical challenges remain in the design of the FT reactor and catalyst
- Laboratory experiments to further improve conversion and light olefin yield, e.g. by product recycling
- Process simulation and kinetic modelling to help with the design problems

VTT

beyond
the obvious

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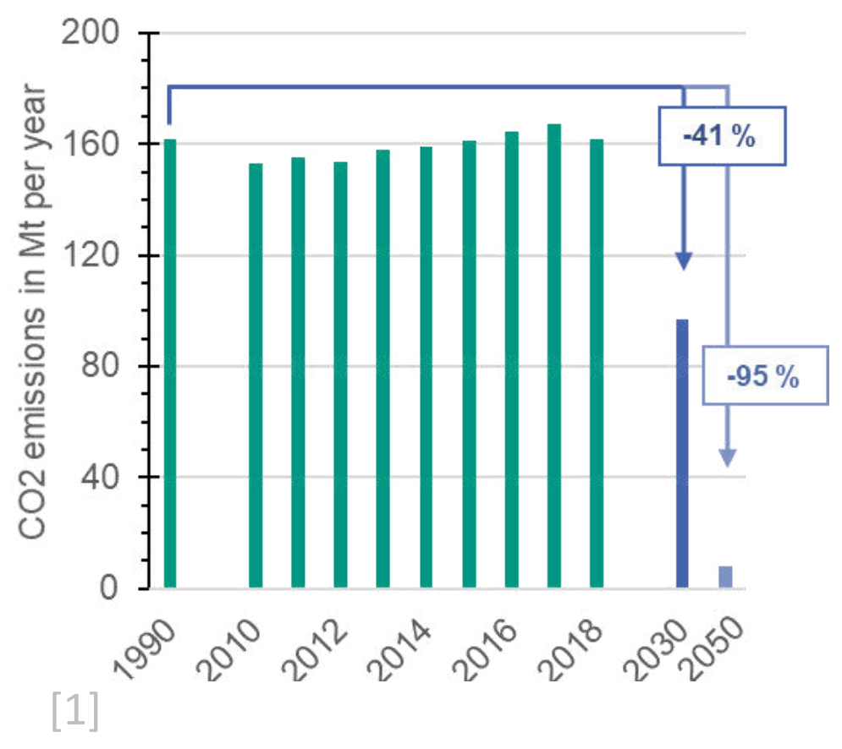
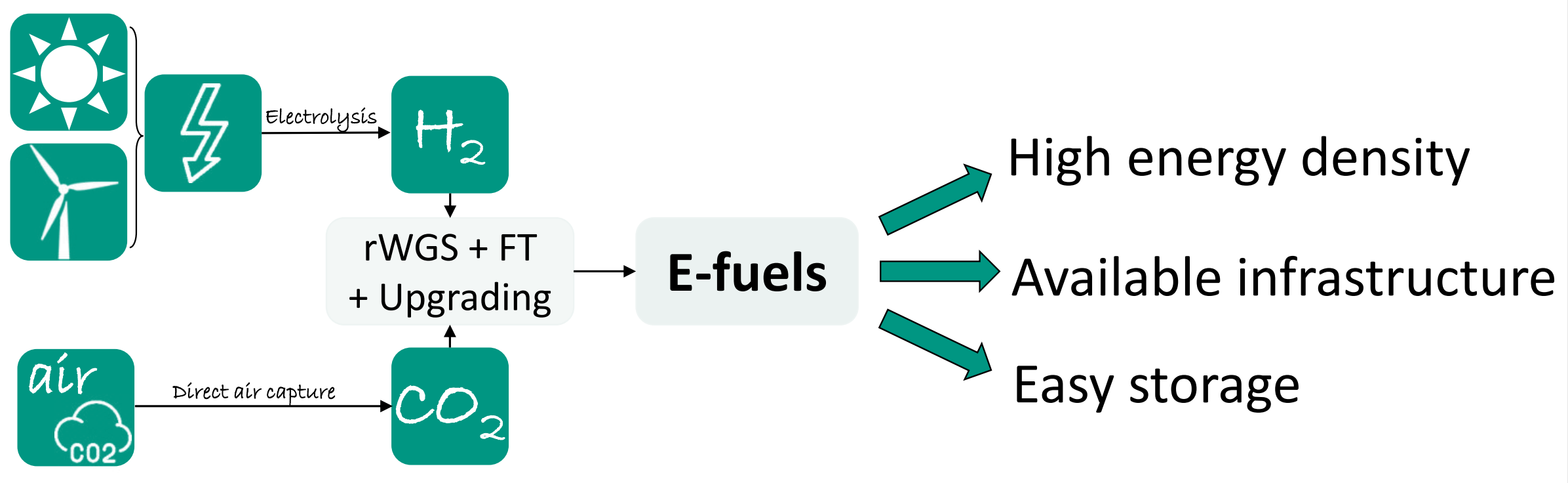
Defossilizing the Aviation Sector with Synthetic Fuels: Production of Aviation Gasoline

Dorela Dhamo, Jannis Kühn, Michael Rubin and Roland Dittmeyer

Institute for Micro Process Engineering

MOTIVATION AND RESEARCH QUESTION





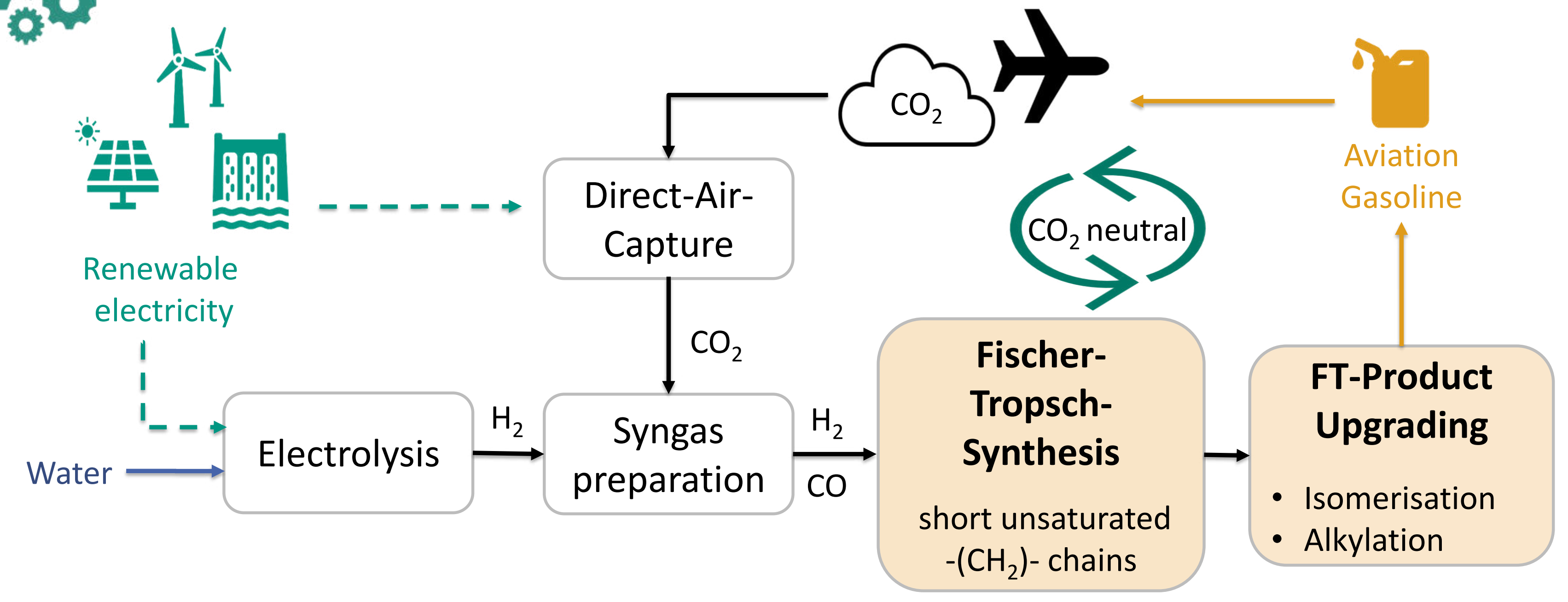
Fuel production from carbon dioxide and renewable electrical energy.

Global goal: Significant CO_2 reductions in the aviation sector using sustainable aviation fuels.

State of the art: **Low Temperature Fischer Tropsch route** fits the best for the production of kerosene, **unbranched hydrocarbons**. For aircrafts with piston engines fuels **branched hydrocarbons, with a high octane number**, are required. Which is the best **synthesis route** for fuels with a with octane number?

Idea: Production of **high octane** fuels through **High-Temperature-Fischer-Tropsch**, **Isomerization** and Dimerization.

APPROACH

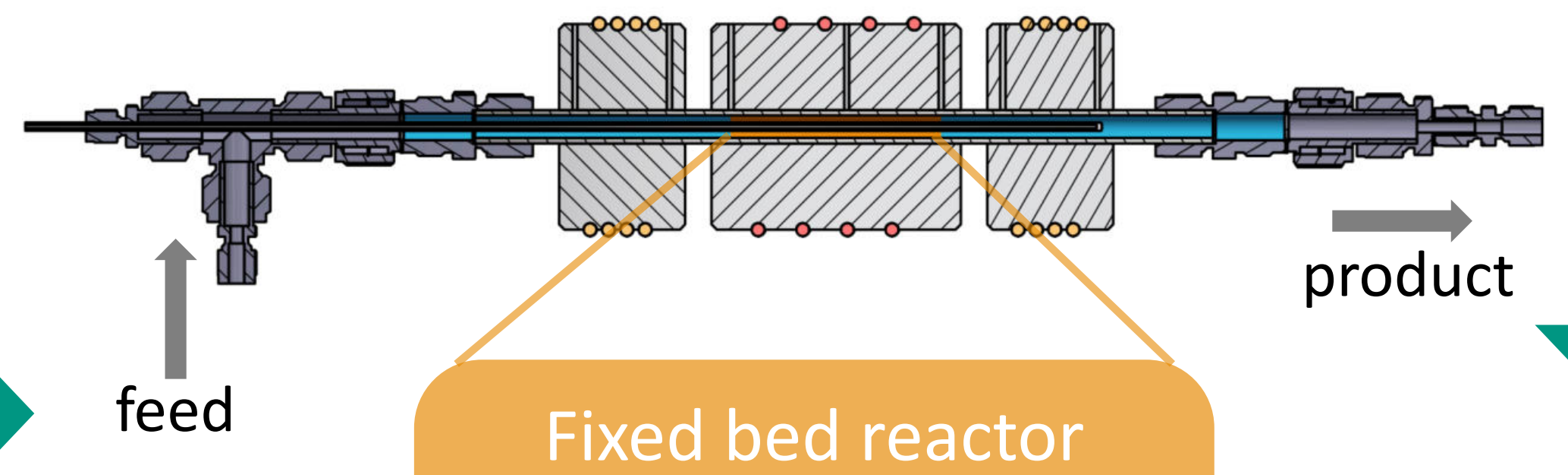


CO_2 + Water → CO + H_2 → Butene → Isobutene → Isooctane → Aviation Gasoline

- Optimization of the High-Temperature-Fischer-Tropsch synthesis → **high butene selectivity**
- Optimization of the isomerization reaction → **high isobutene selectivity**
- Coupling of High-Temperature-Fischer-Tropsch and isomerization steps:
  - → Understanding the influence of the other FT products on the isomerization step
  - → **High isobutene selectivity**
- Kinetic modelling and simulations

EXPERIMENTS

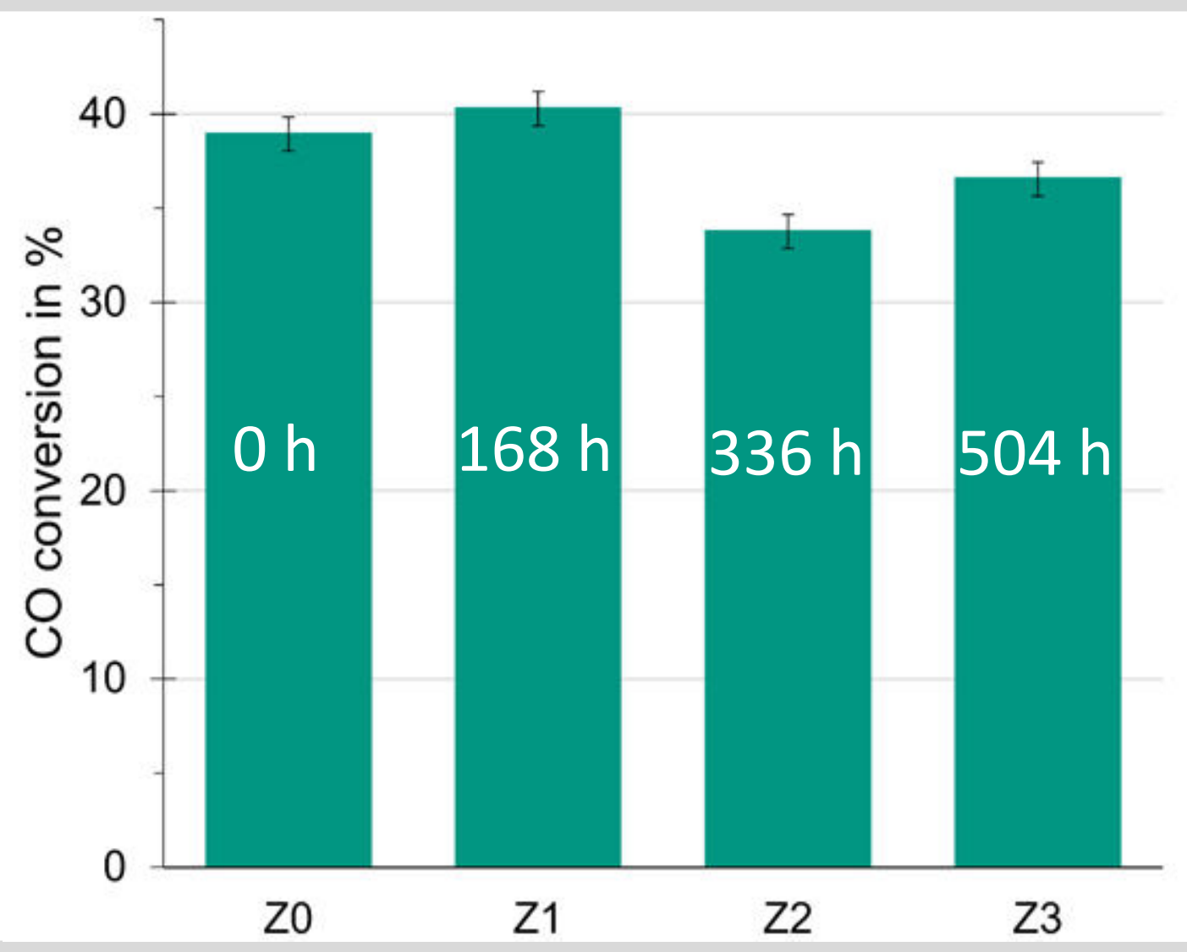
Catalyst:	Fe-Cu-K/SiO_2 commercial
Particle size:	100-200 µm



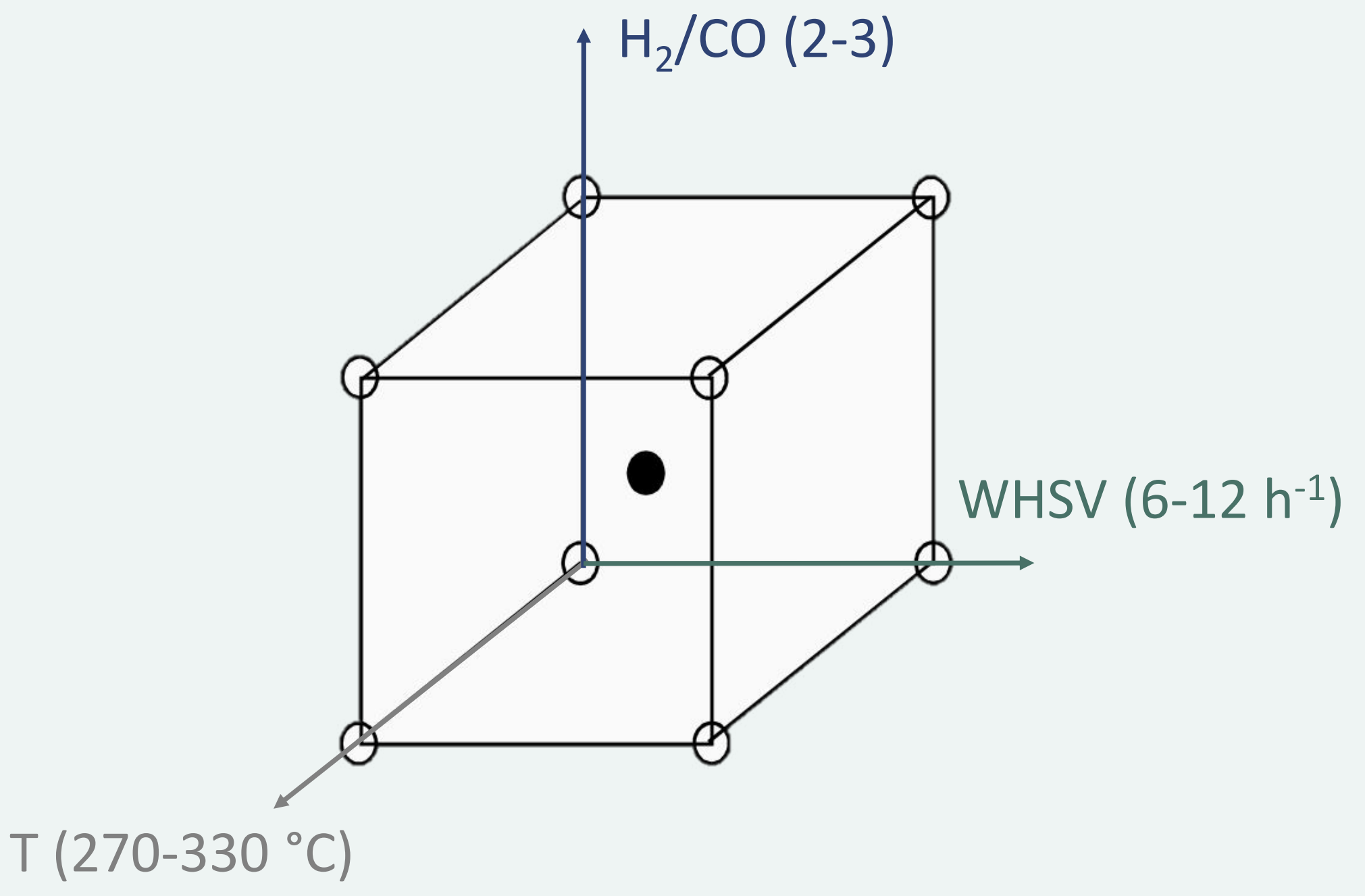
Fixed bed reactor
80 mm reaction zone
0.7 g catalyst
Dilution Cat:SiC =1:3

Catalyst activity:
Conversion measurements
@same condition (T=300 °C, p=20 bar, H_2:CO= 2.5, WHSV=9 h^{-1})
@different stages over the entire experiment period

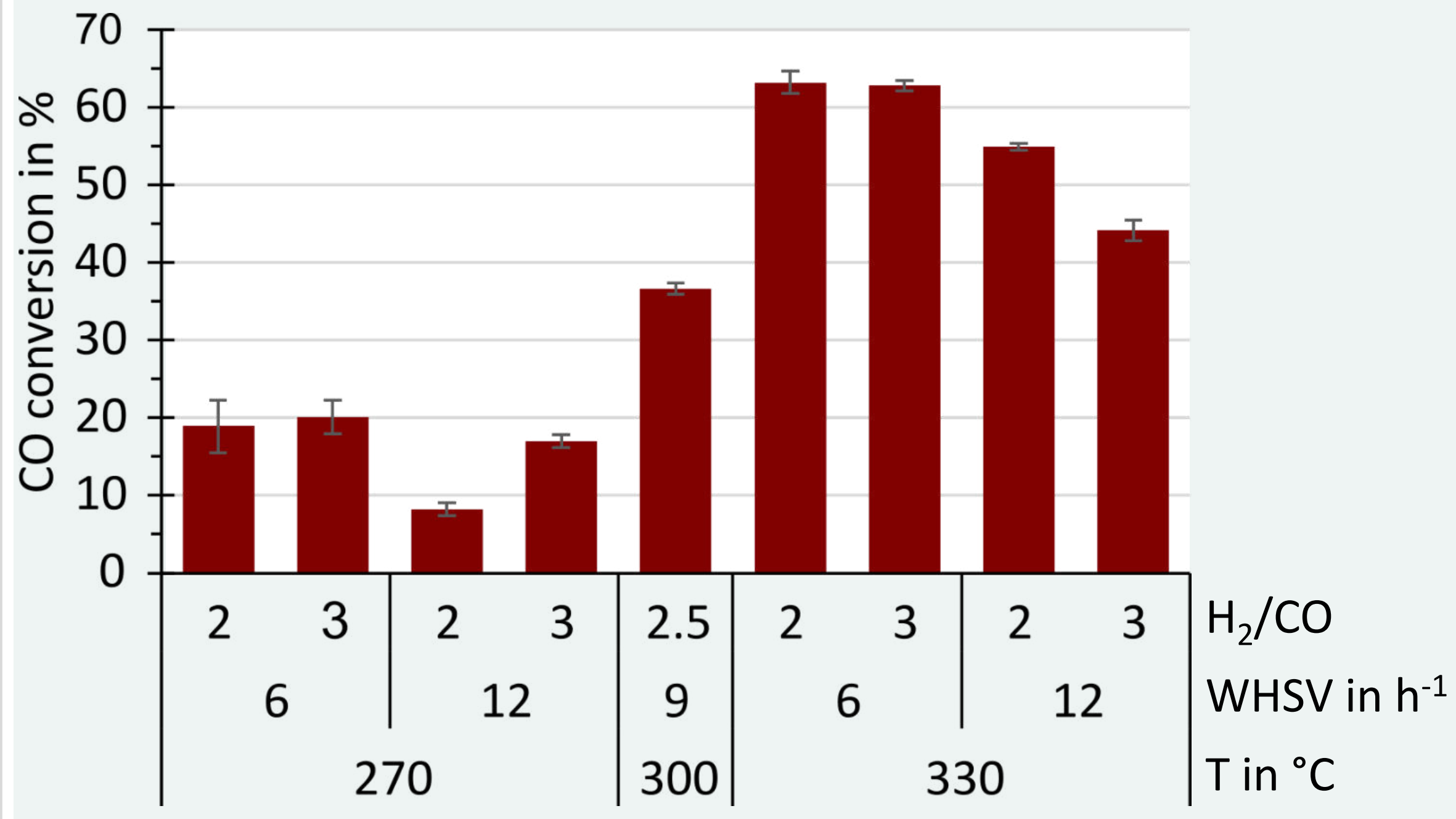
→ No significant deactivation



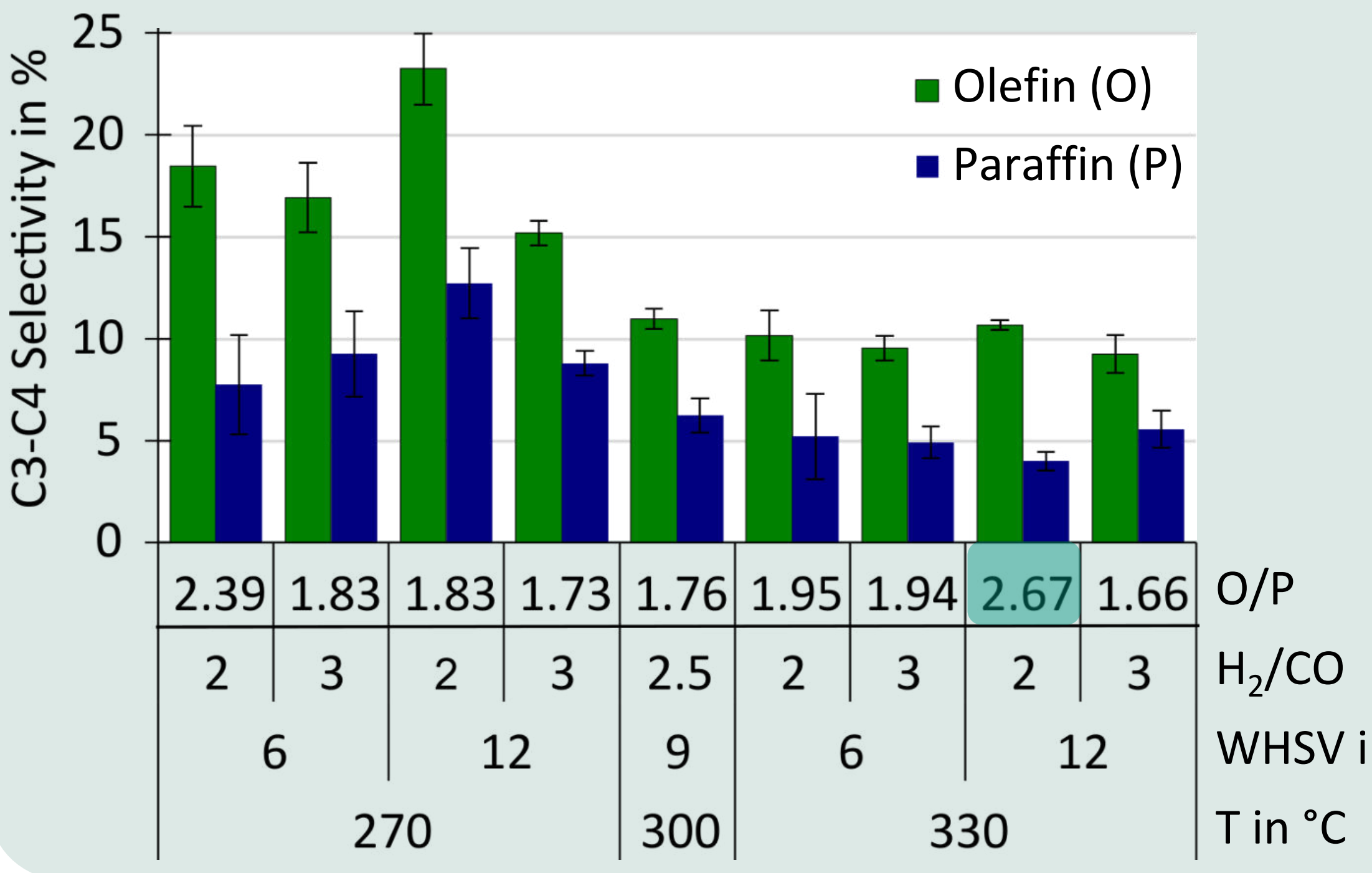
RESULTS



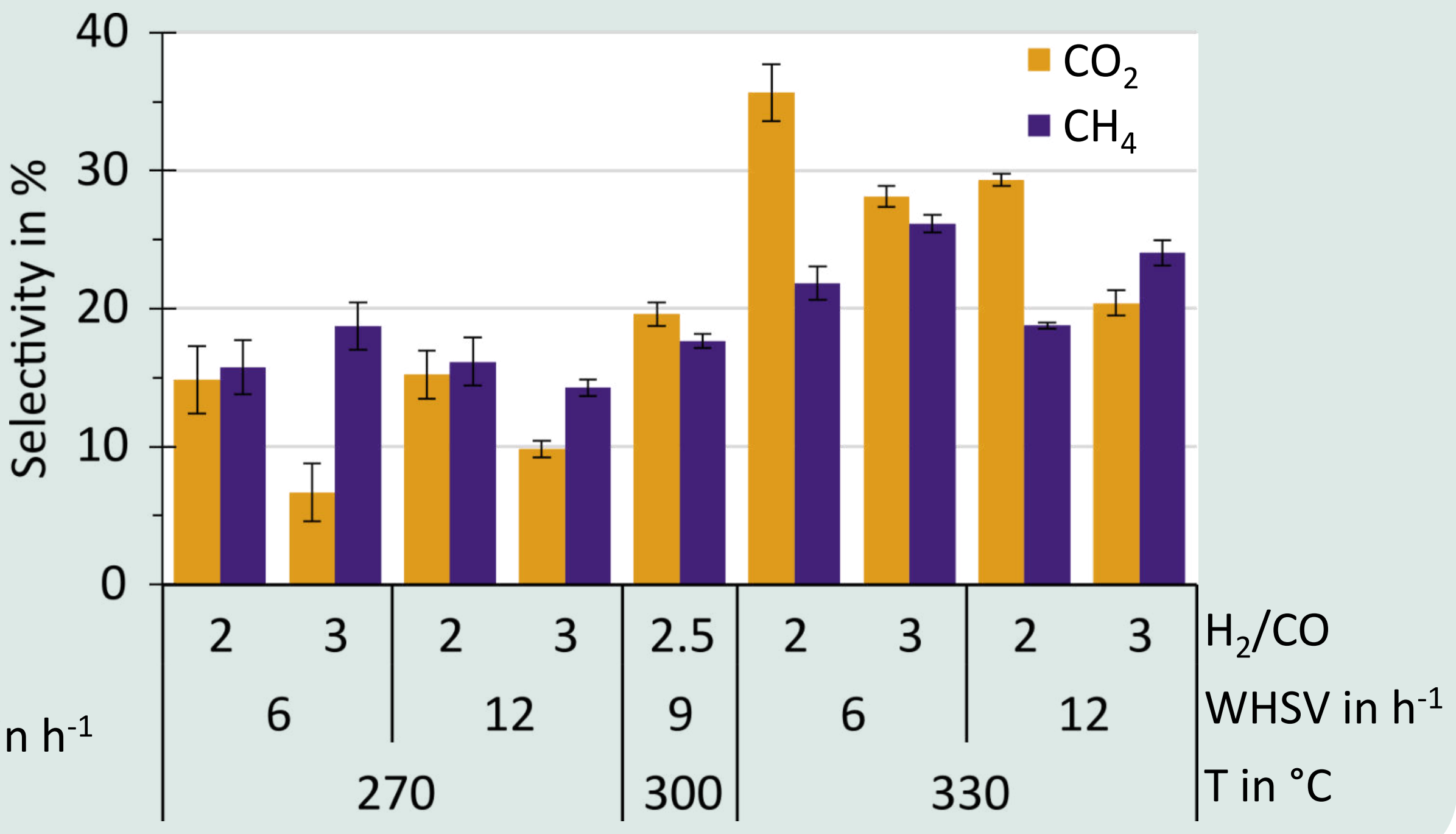
- **Conversion**



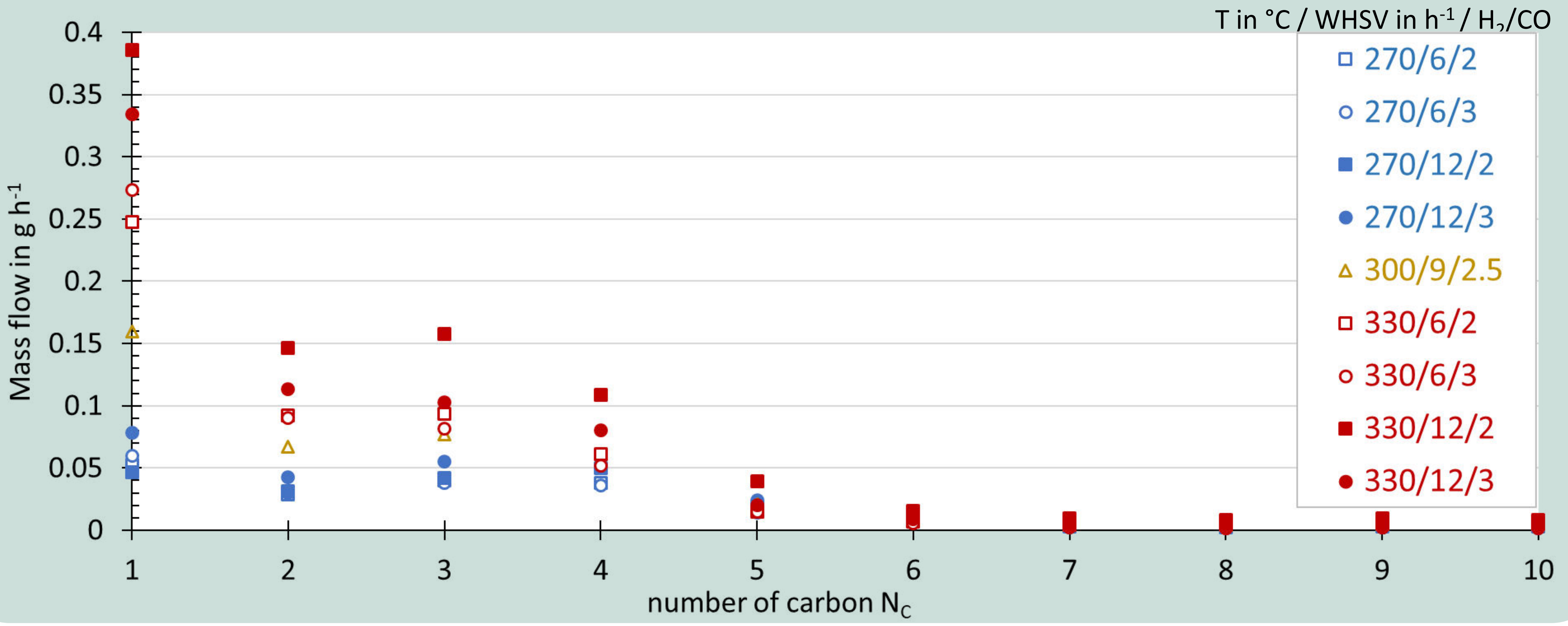
- **Olefin / Paraffin ratio**



- **Side products**



- **Product distribution**



CONCLUSIONS AND OUTLOOK

- High conversion can be achieved at high temperatures and low WHSV.
- At 330 °C the selectivity of C_4-chains compared with C_1-C_3 molecules is lower than at 270 °C. Nevertheless, due to the higher conversion the reaction rate of the C_4 products is higher at higher temperatures.
- Highest olefin to paraffin ratio at high temperatures, high WHSV (therefore short residence time in the reactor) and low H_2/CO ratio.
- There are two side products produced at significant amounts: CO_2 and CH_4

- CO_2 selectivity increases with increasing temperature
- CH_4 selectivity increases with increasing temperature and H_2/CO ratio

- Investigate the CO_2 effect, by adding CO_2 as feed.
- Decrease CH_4 selectivity by decreasing H_2/CO ratio

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[1] Source: Treibhausgas-Emissionen in Deutschland | Umweltbundesamt

Green “Future Quota” for power-to-X fuels like green hydrogen and jet fuel

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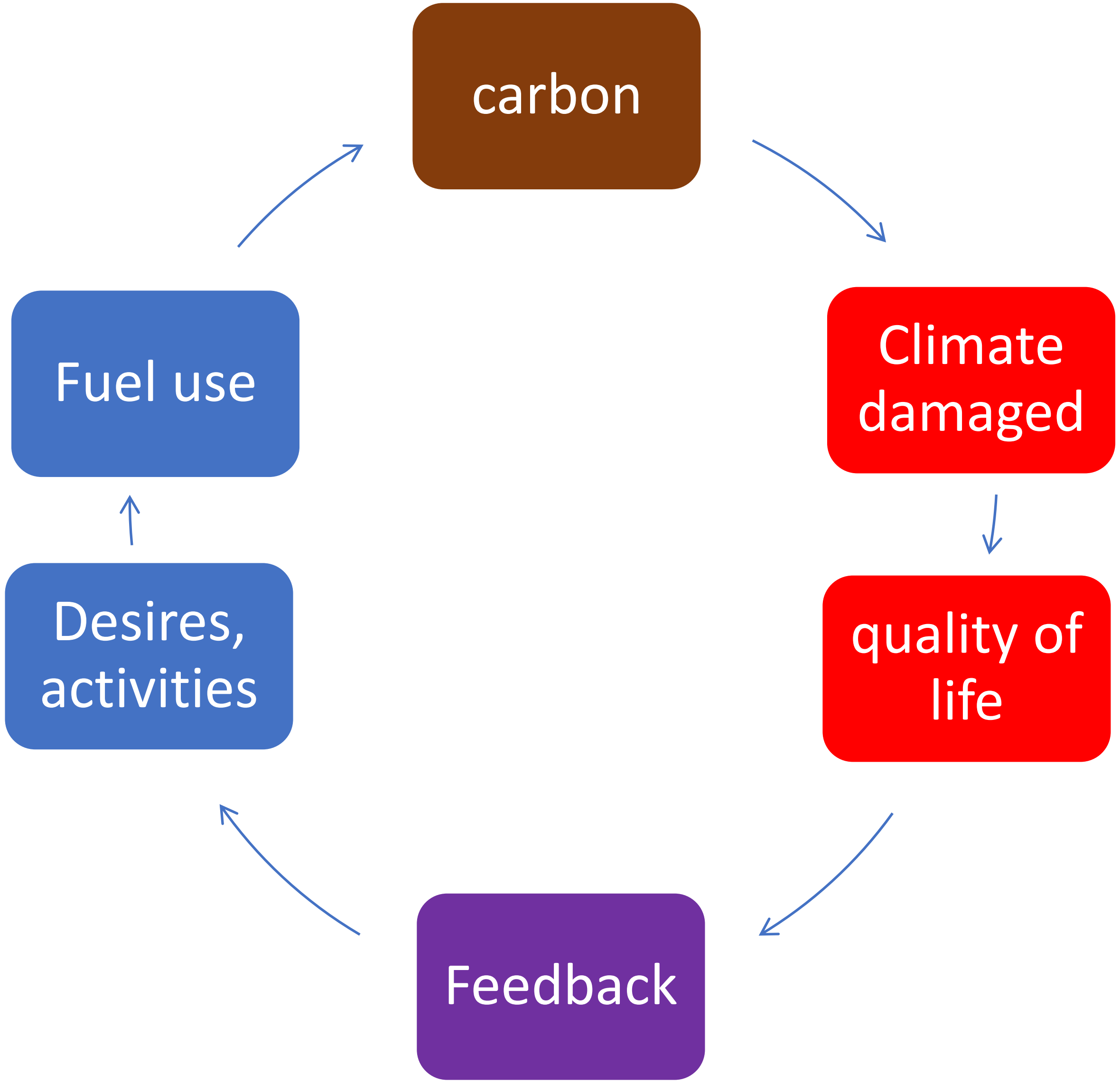
Externalities

- Climate change affects other people
- State must protect from adverse effects



carbon

Climate damaged

quality of life

Feedback

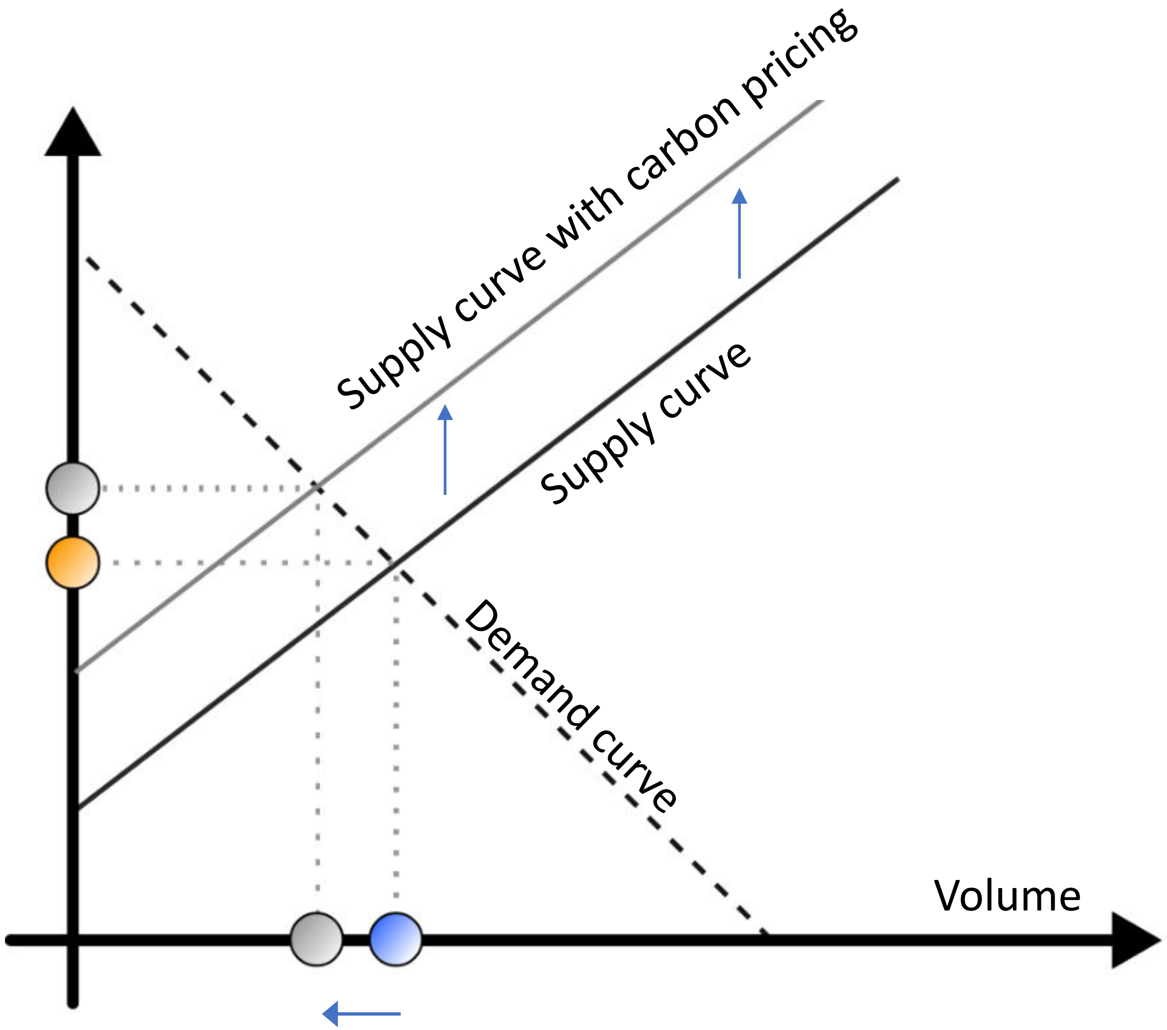
Desires, activities

Fuel use

Economists prefer carbon pricing

- Pigou pricing: activities with external damages shall be priced (taxed), so that the damage is taken into account by the individual actors (internalised)
- Alignment of individual interest and societal concerns
- Individual decision-making rather than goverment plans
- **Motivation to avoid carbon emissions** rather than motivation to circumvent regulation
- Least-cost avoidance of carbon emissions
- Early actors are keen that carbon pricing will be upheld, so that their investment can be amortized
- Relies on long-term approach, neutralized or adversely affected by other policies

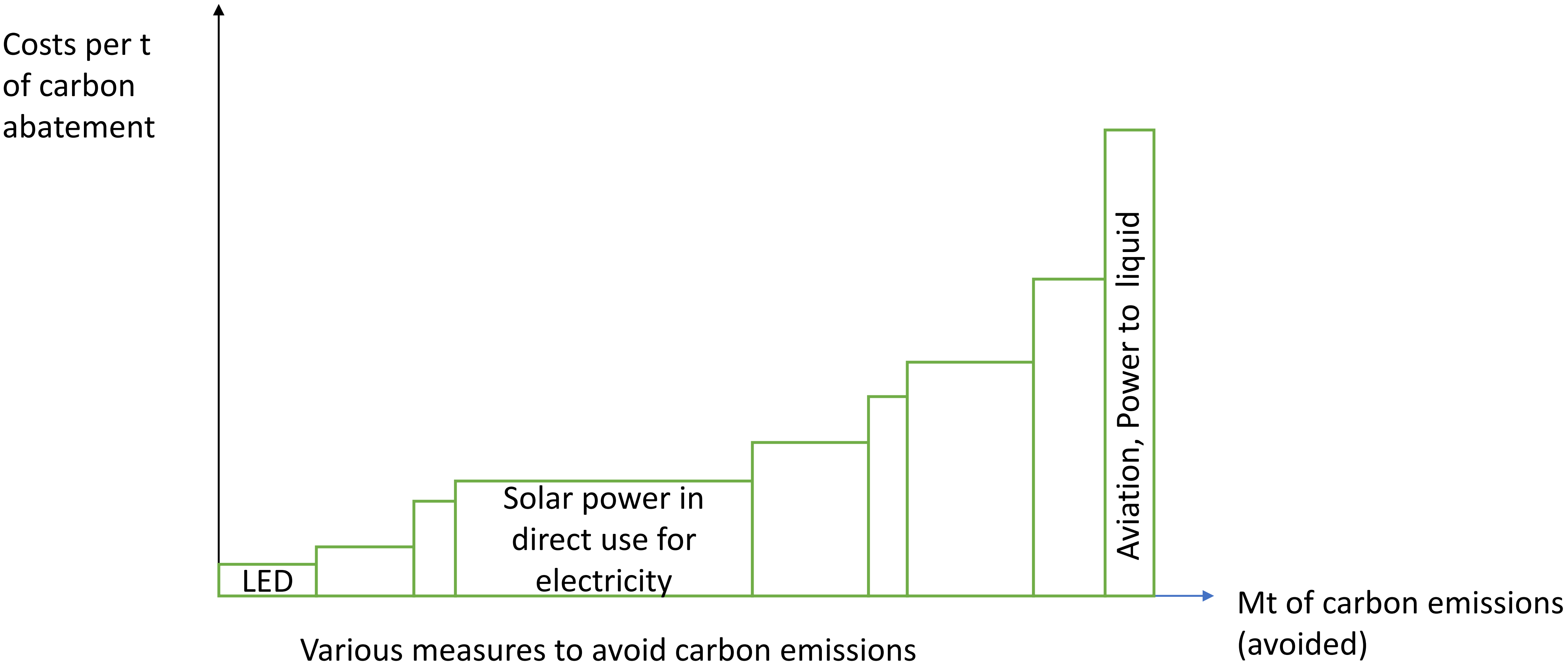
Price equilibrium with carbon pricing



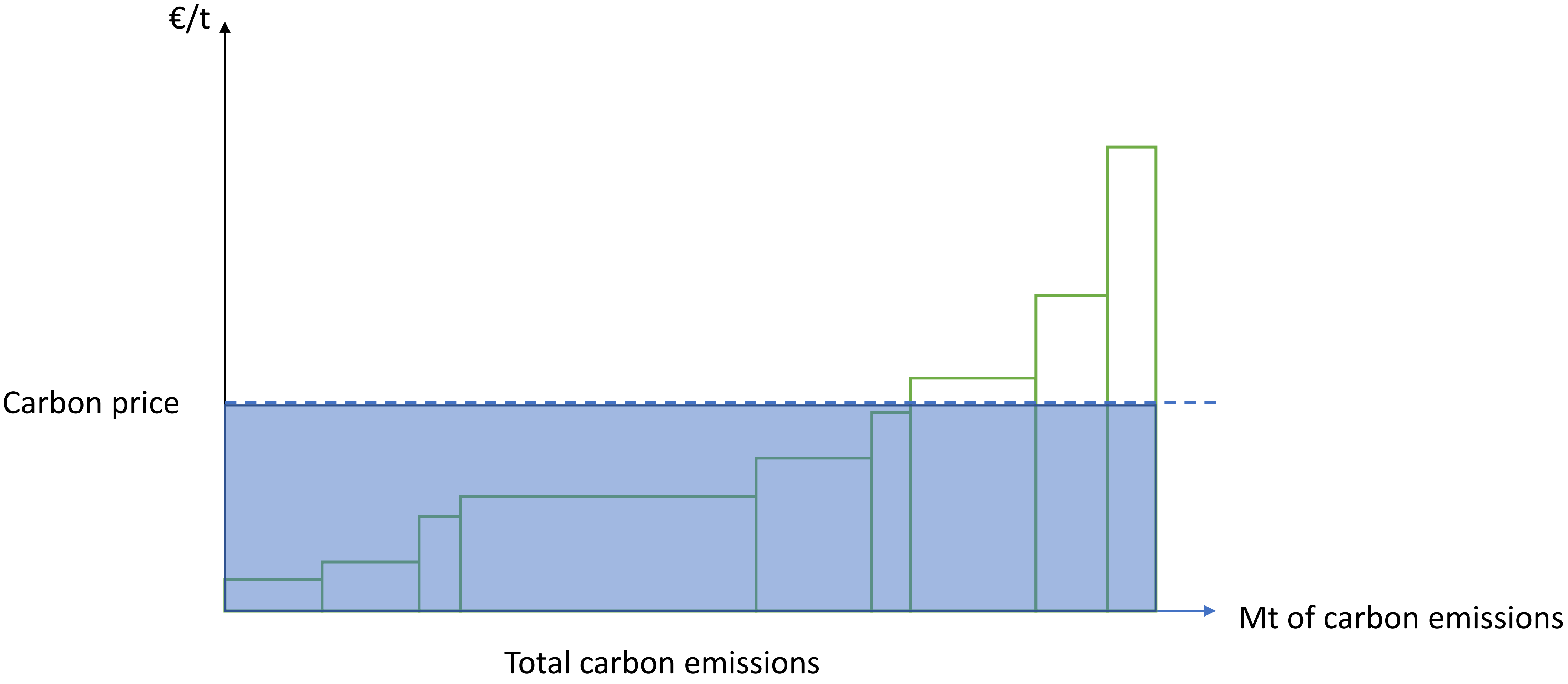
Volume is reduced due to carbon pricing

from wikipedia, creative commons

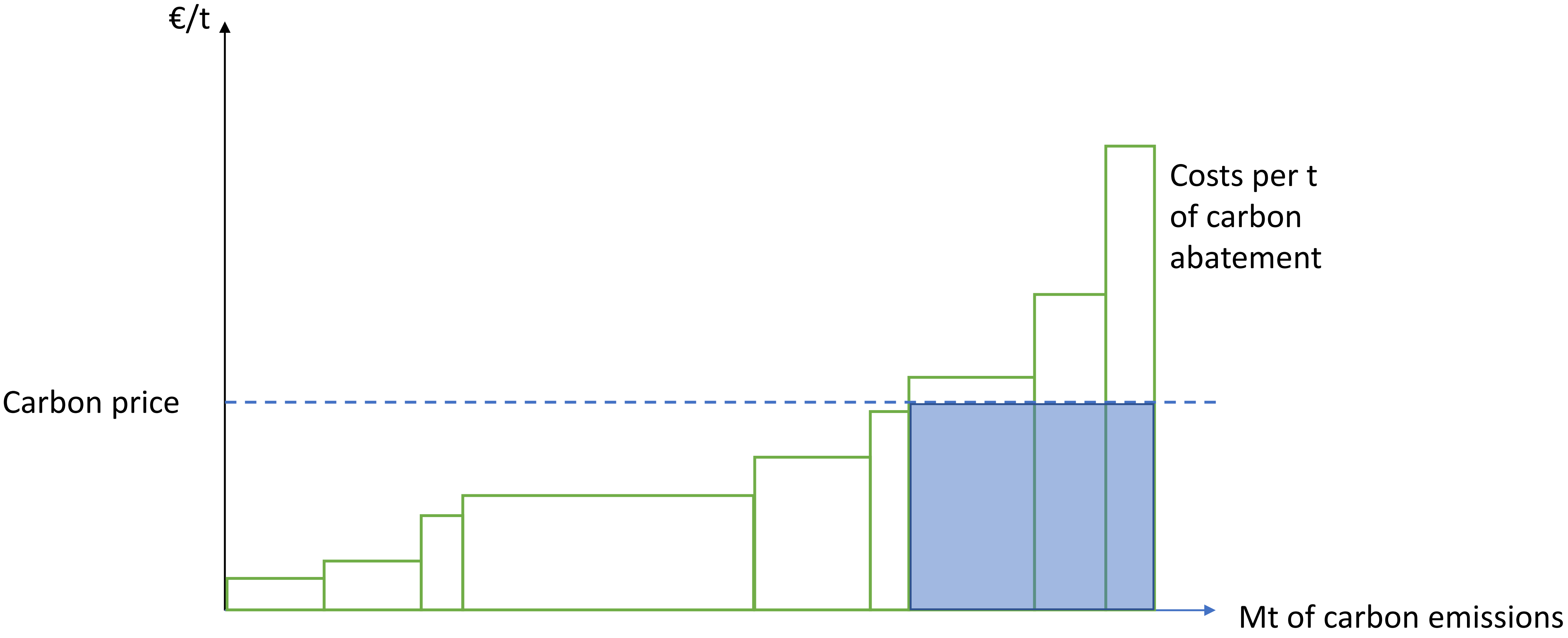
Simplified example of total carbon emissions and their respective abatement options and costs



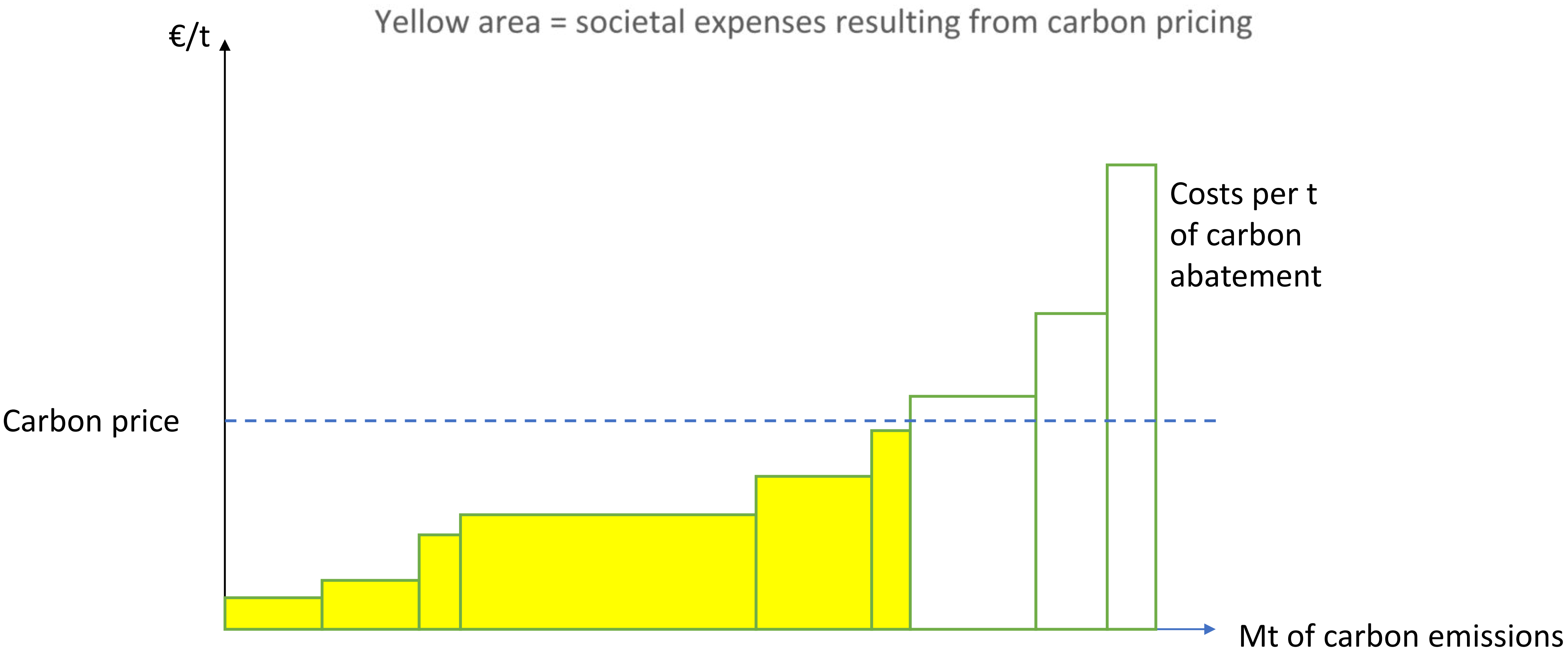
Perceived (short term) costs of carbon emission pricing



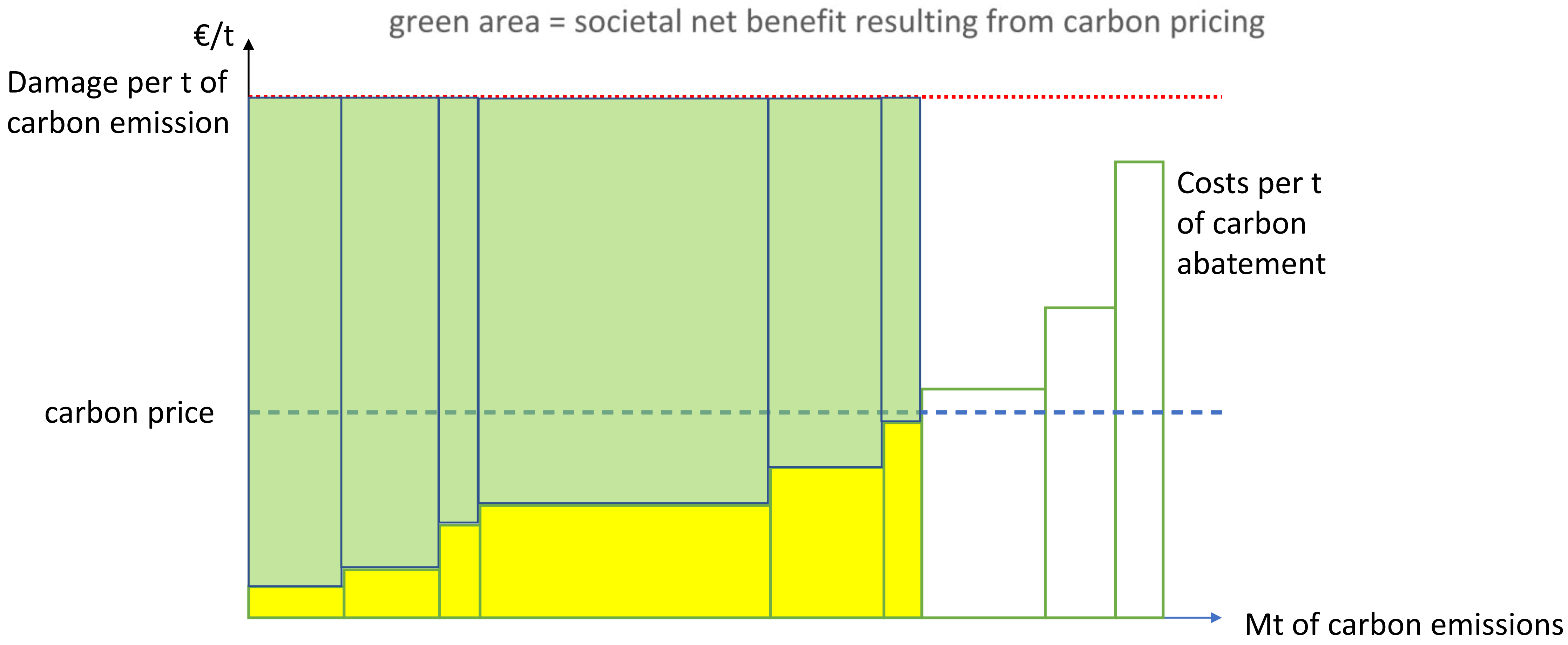
Carbon taxes being paid



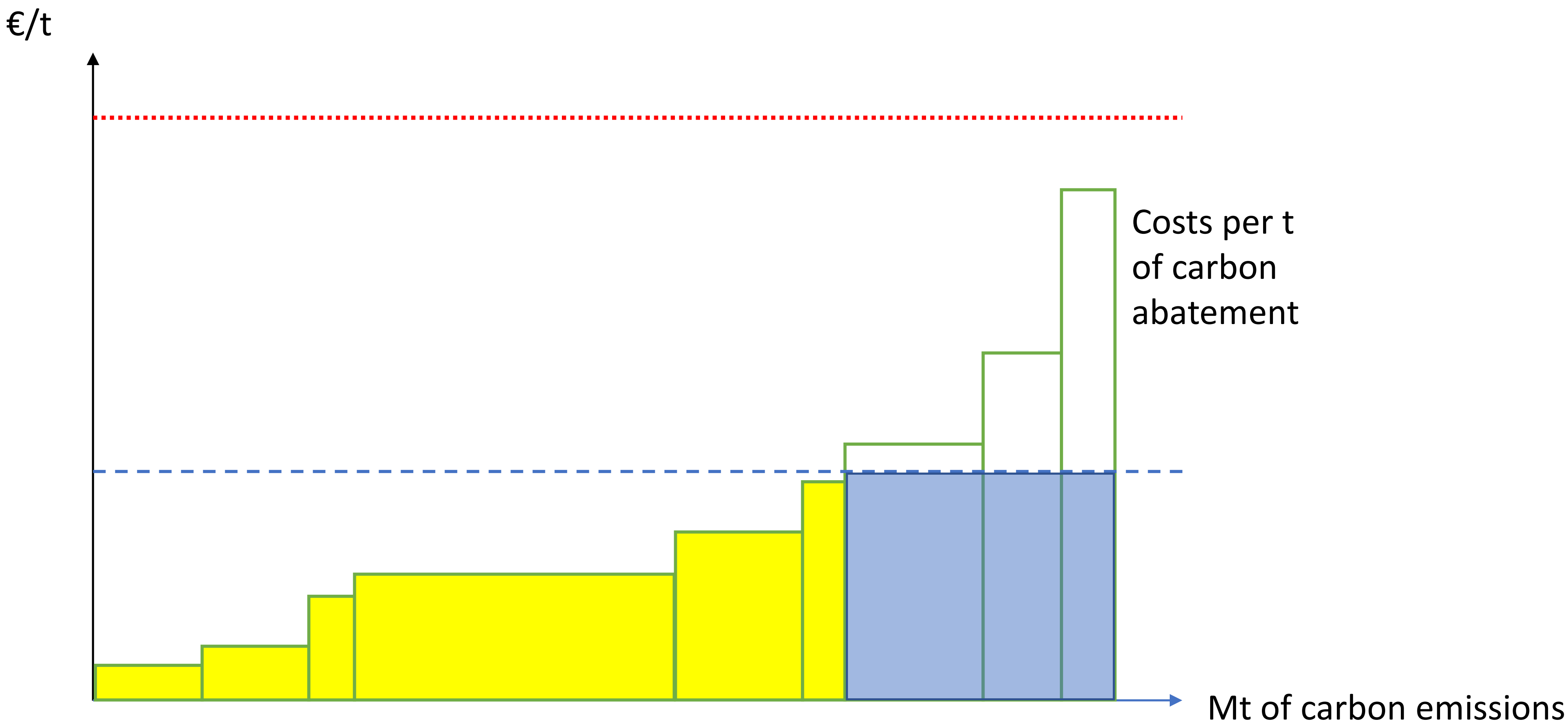
Societal expenses from carbon pricing



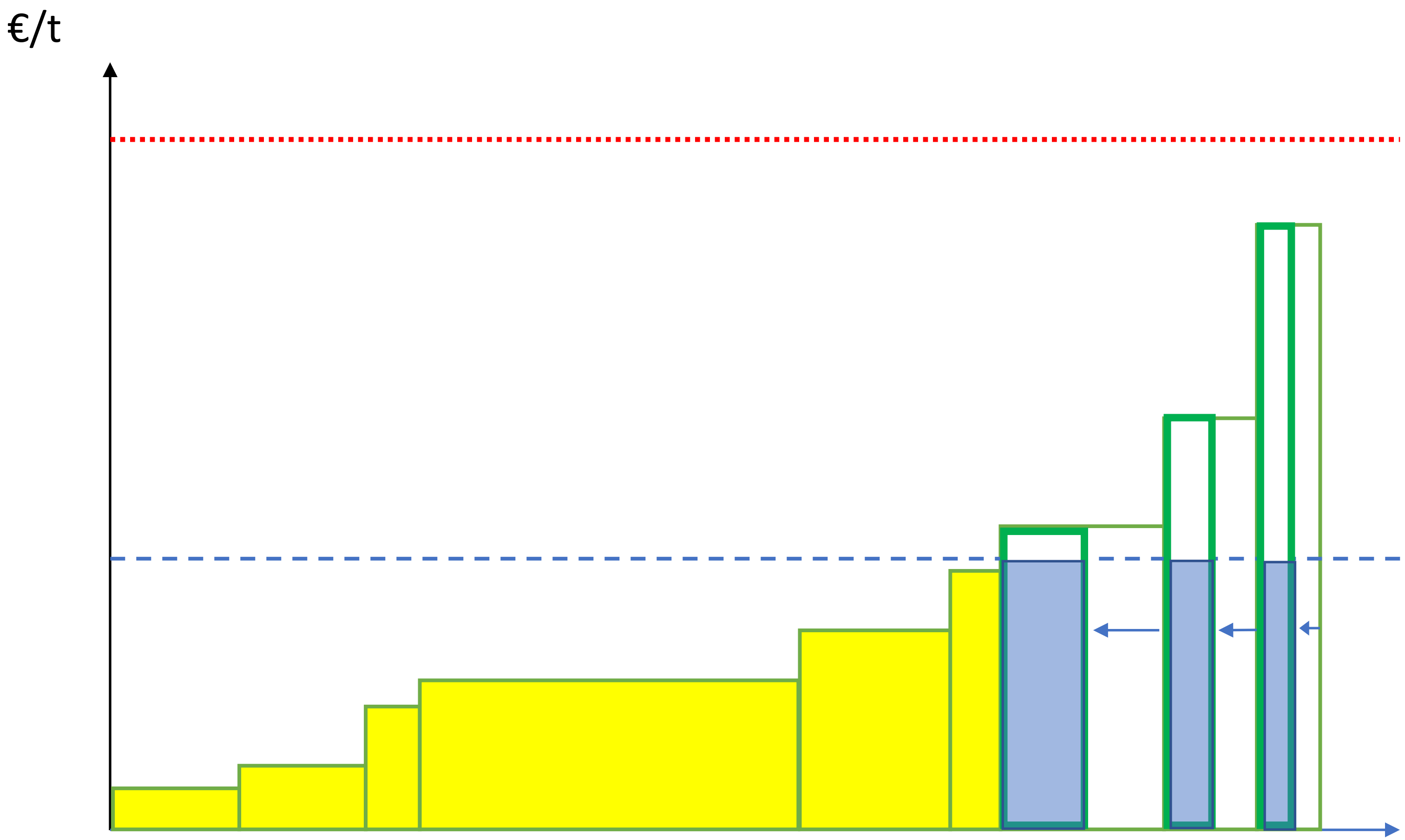
Societal benefit from carbon pricing



Carbon taxes are the unwanted part of carbon taxation

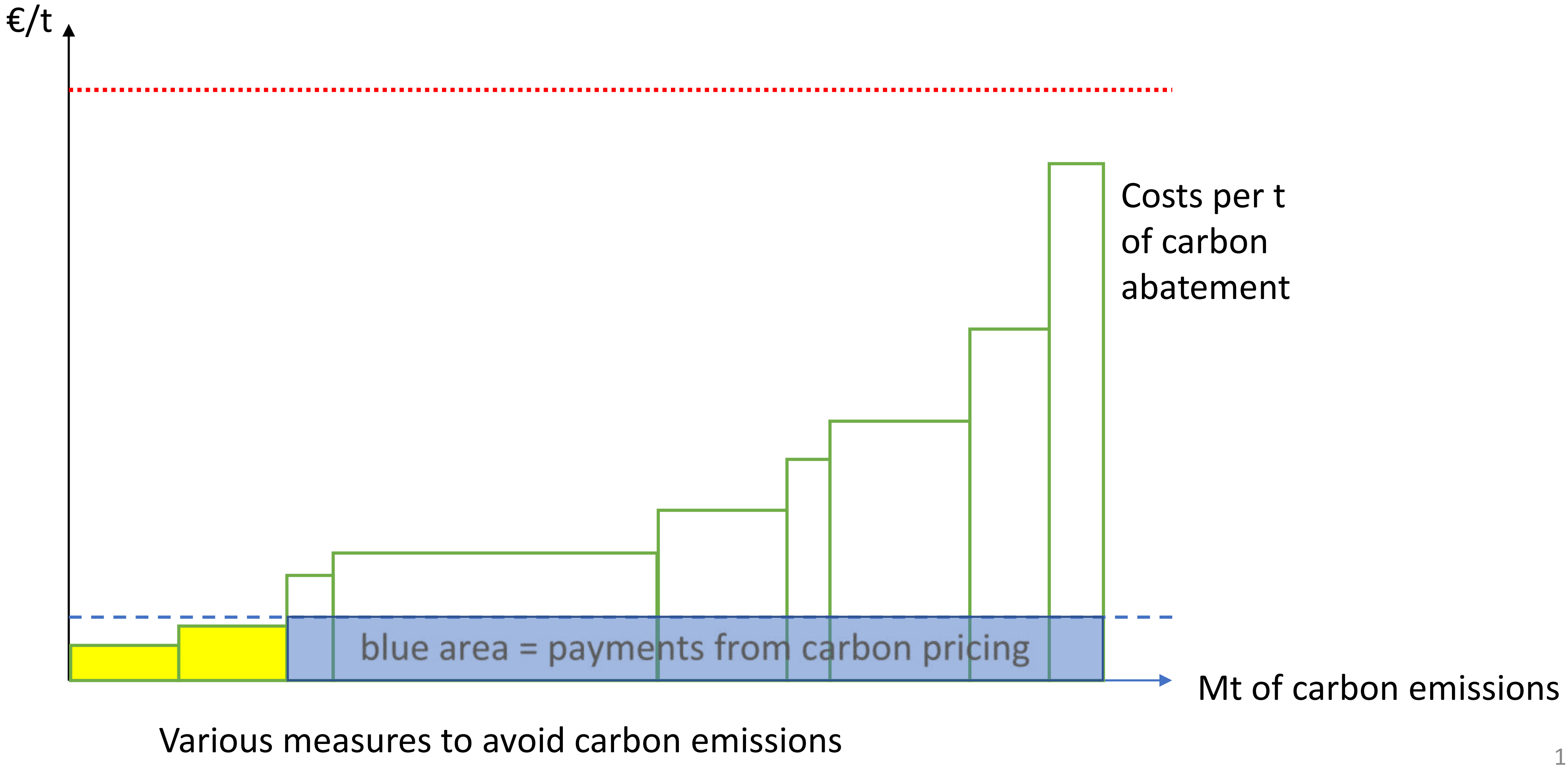


It looks a better when taking into account that activities that were not yet "greened" are reduced by the (intended) cost and price effect that is produced by the quota

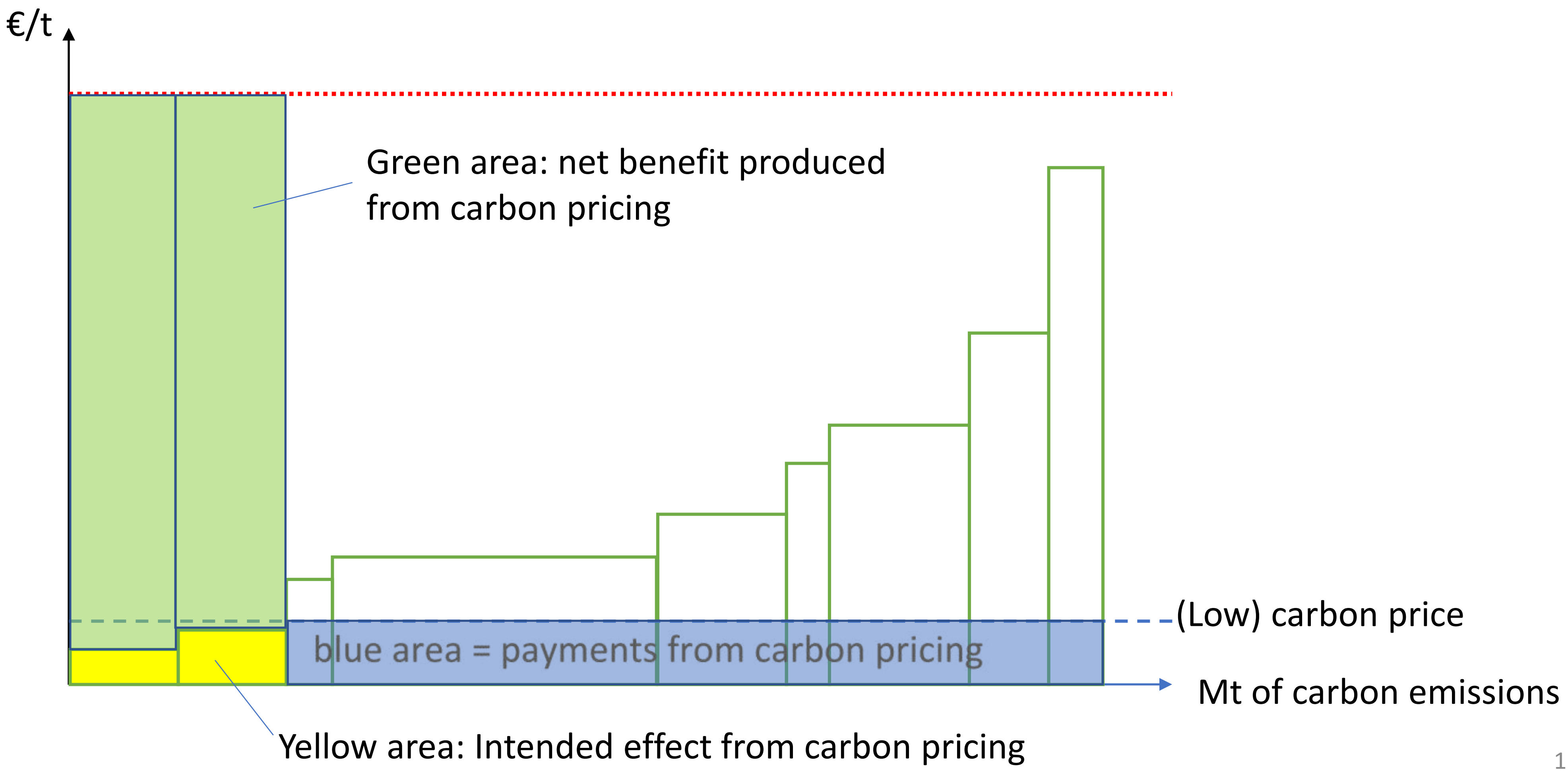


In a more puristic view, efforts to reduce the use of activities and products that were not yet greened by technology also come at a cost, and their reduction is part of the measures that would form the yellow stages in ths graph

Low carbon price level: The unwanted part of the carbon tax income may dominate financially



Societal benefit may nevertheless be large also with a low carbon price level



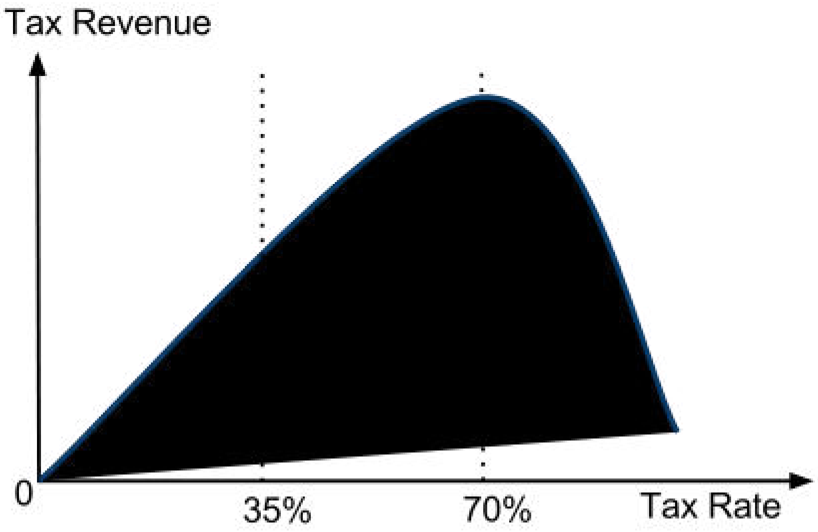
How to use the „excess money“?

Disagreement on use of carbon tax income

- Classical economists/conservatives: lower taxes in income, reduce inefficiencies that result from these taxes (double benefit)
- Social democrats/liberals/greens: make sure poor are not burdened by costs, support for poor or uniform per capita reimbursement that would lead to net benefit for most poorer sections of society
- Or fund state decarbonisation programs from carbon taxes,
  - to give more „meaning“ to the tax income
  - income generation as primary intention
  - but with adequate carbon tax, no need for additional stimulus
  - with progress of decarbonisation, taxes decrease, more expenses for programs

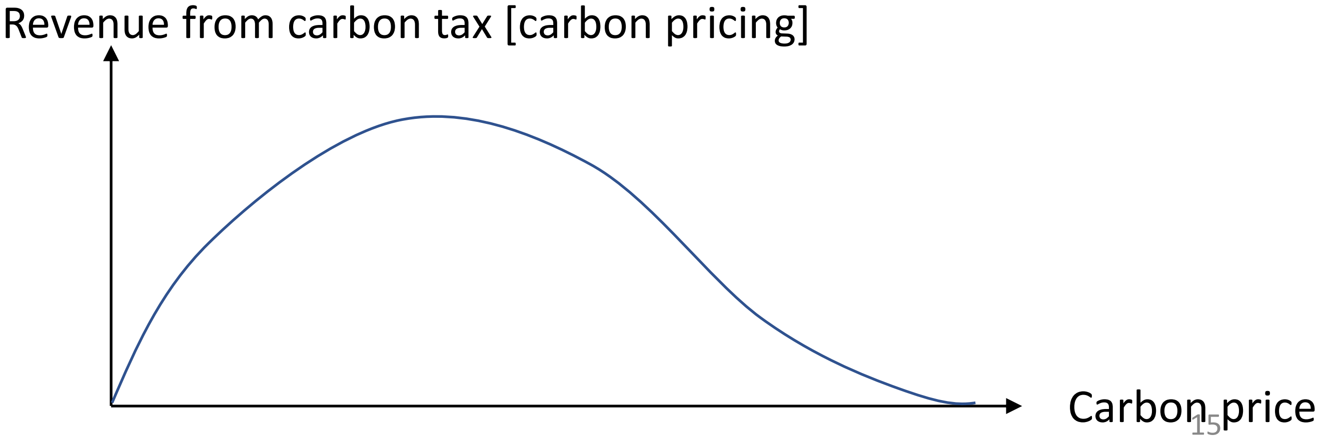
Limitation: zero carbon will lead to zero carbon tax

Laffer curve for taxation of income



from wikipedia, creative commons

Carbon tax will no more yield any return when it is sufficiently high to stop all carbon emissions



Broad definition of Quota

Obligation to provide or use A in proportion Q to use, sale or production of B

Definition of Quota $A \geq Q * B$

B = adverse, obliged activity or product being used (e.g. fossil fuel)

A = activity or product to be supported (e.g. e-fuel)

More elaborate $A(t_2) > Q(t_1) * B(t_1)$

t_1 = obligation period

t_2 = fulfilment period(s)

For an immediate blending obligation, $t_1 = t_2$.

The quota $Q(t_1)$ can increase over time.

Advantages of quotas

- Suitable for gradual, controlled increase

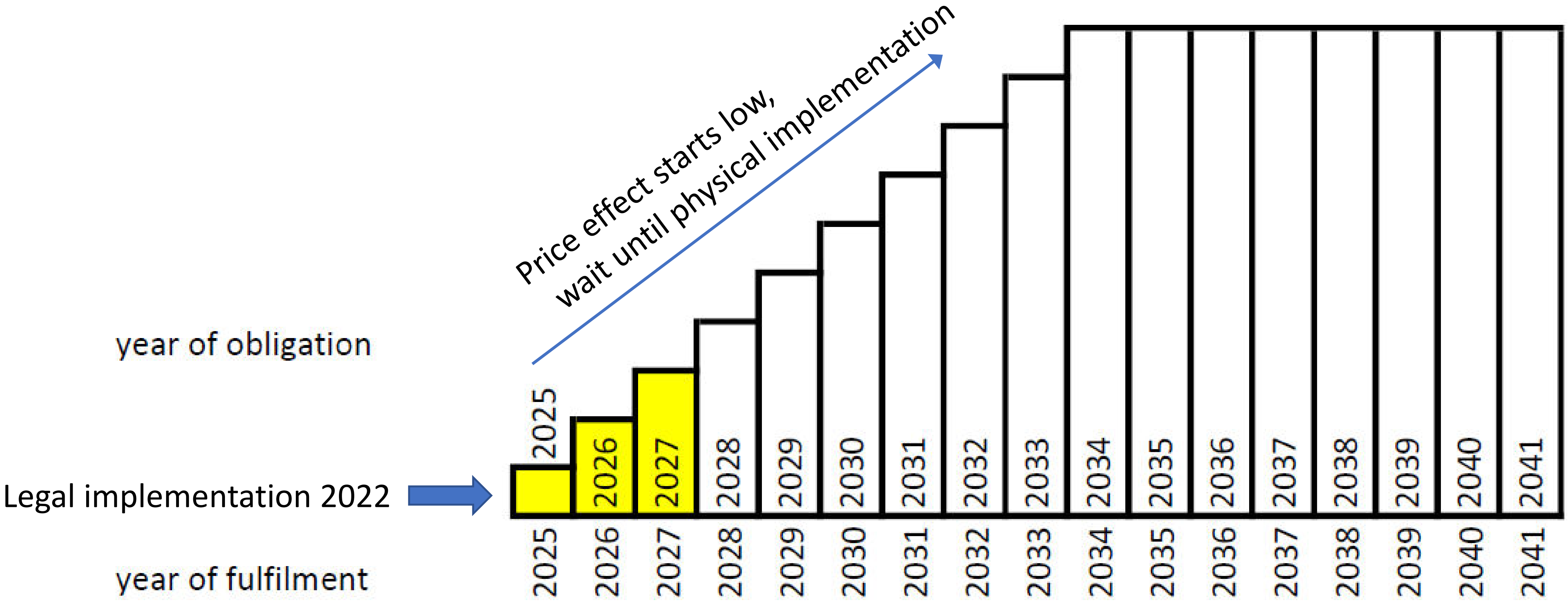
– whereas carbon prices or feed-in tariffs may lead to no activities, when below costs, and rather quick transition, when above costs

- Even when initial costs per unit are high, transition can be initiated without similarly high overall carbon prices
- Quota most appropriate for technology with falling costs – otherwise prefer carbon pricing
- Quotas work on both fronts:
    - Implementation of „greener“ technology
    - Less use of old technology through price and demand effects

Disadvantages of quotas

- Cost for fulfillment of quota is not equivalent to cost load that should be achieved in accordance with cost of pollution
- Costs for fulfillment of quota raises with quota and with time, while the cost load should be the highest when the quota is still low and the share of the polluting product B is high.
- adequate lead time must be allowed from legal implementation to start of fulfillment (if no small country):
  If fulfillment be at the same time of consumption, no obligation and incentive during lead time

Classical quota, growth according to „meaningful“ targets



Variants of Quota:
Time and location of fulfillment

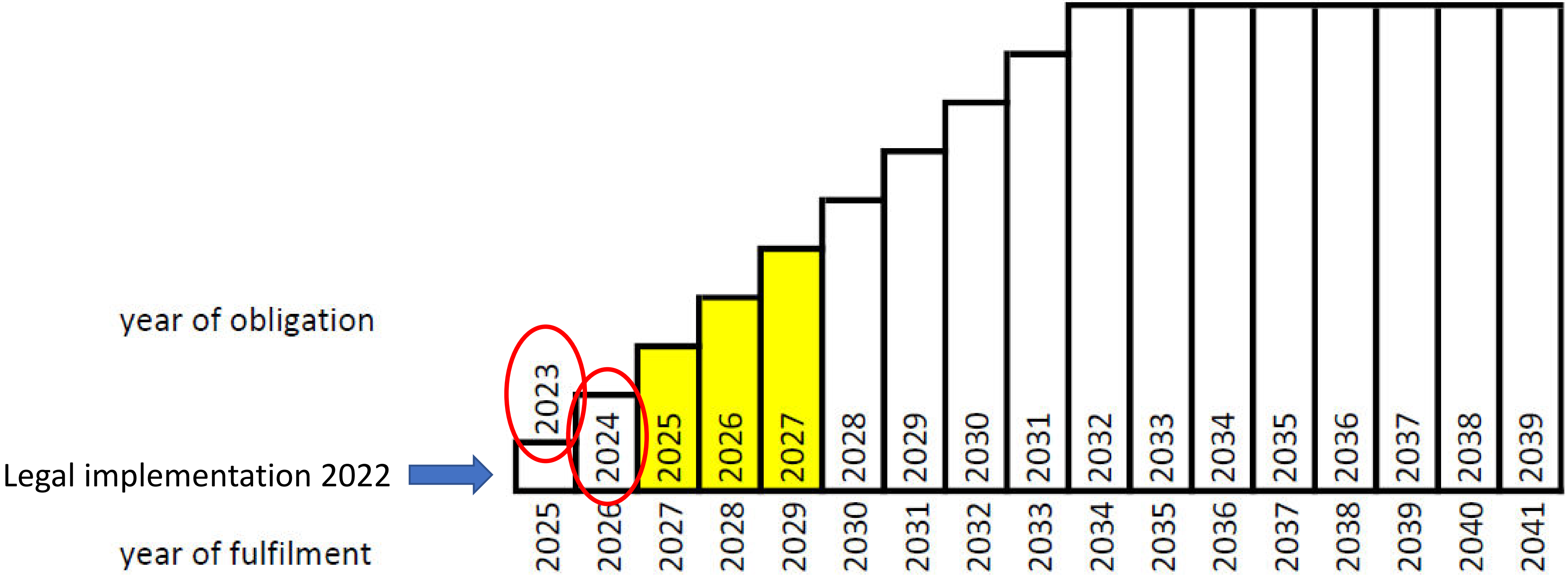
- Fulfill at same time of prior to use of „B“
- Fulfill after a lead period
- **Fulfill during a multi-year period**
- Fulfill within lifetime of equipment

- Fulfill at same place or in same market
- Fulfill anywhere, if physically connected (similar to green power)
- Fulfill anywhere

Variants of Quota: type of product supported

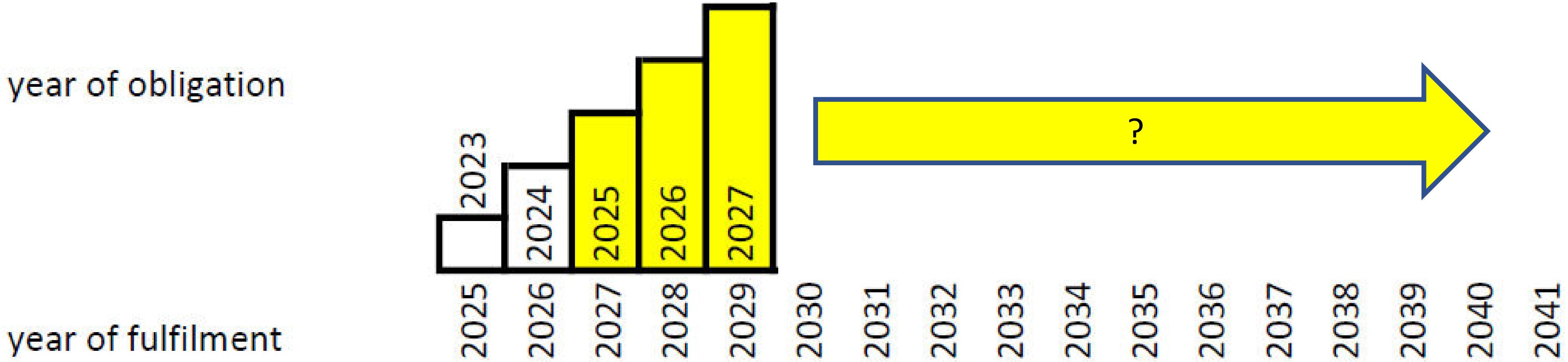
- „A“ can be an immediate replacement of „B“
  (e.g. Q is a ratio of hydrocarbon e-fuel relative to kerosene).
- „A“ can be an investment to replace „B“ (e.g. obligatory investment to produce e-fuel).
- „A“ can be a replacement of the energy content of „B“ (e.g. including hydrogen that may be suitable for aircraft of the future)
- „A“ can be a replacement of „B“ in a broader sense (e.g. an amount of non-fossil long-distance transport, either land-based or by aircraft)
- „A“ can support the replacement of „B“ (e.g. research in the production of e-fuel and aircraft equipped to use novel e-fuels

Quota with „delayed“ fulfillment



The delayed fulfilment allows for an **earlier** price-derived effect on the consumption of the problematic goods

Quota abolished: Who pays for capacity?



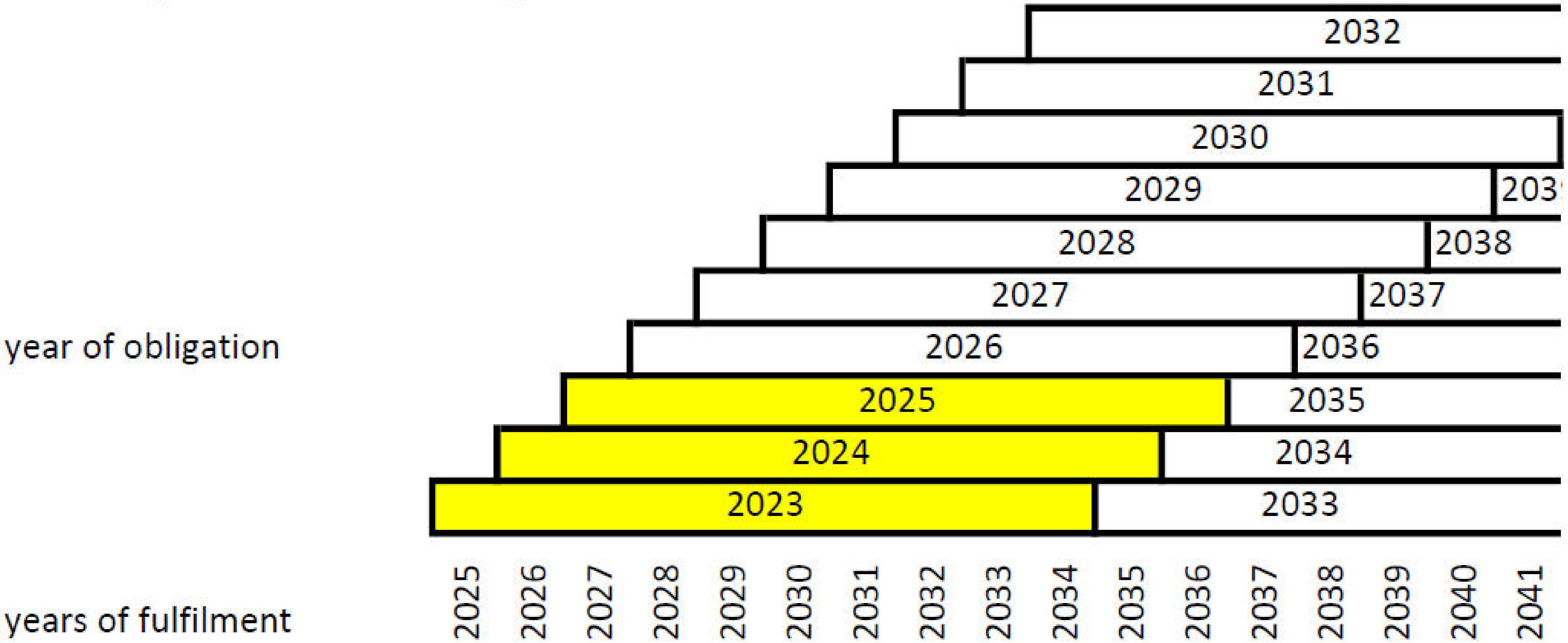
- Inadequate risk for providers of quota-fulfilling products in case of policy change.
- Also high risk in case of lowered costs for fulfillig quota with newer equipment

Reducing costs lead to higher costs

Assumptions:	Cost (year 1)	100 M€
	Lifetime	20 years
	interest, profit	0 %
	capital cost	*5 M€ p.a. for each year 1 to 20 ??*
Also assume	Cost (year 2)	80 M€
	capital cost (year 21)	2 M€ p.a.

Investing in year 1 costs 20 M€ more, loses 2 M€ income in year 21.
Effective costs for utilization of equipment in year 1 are 22 M€.

„Future Quota“: fulfillment over several years

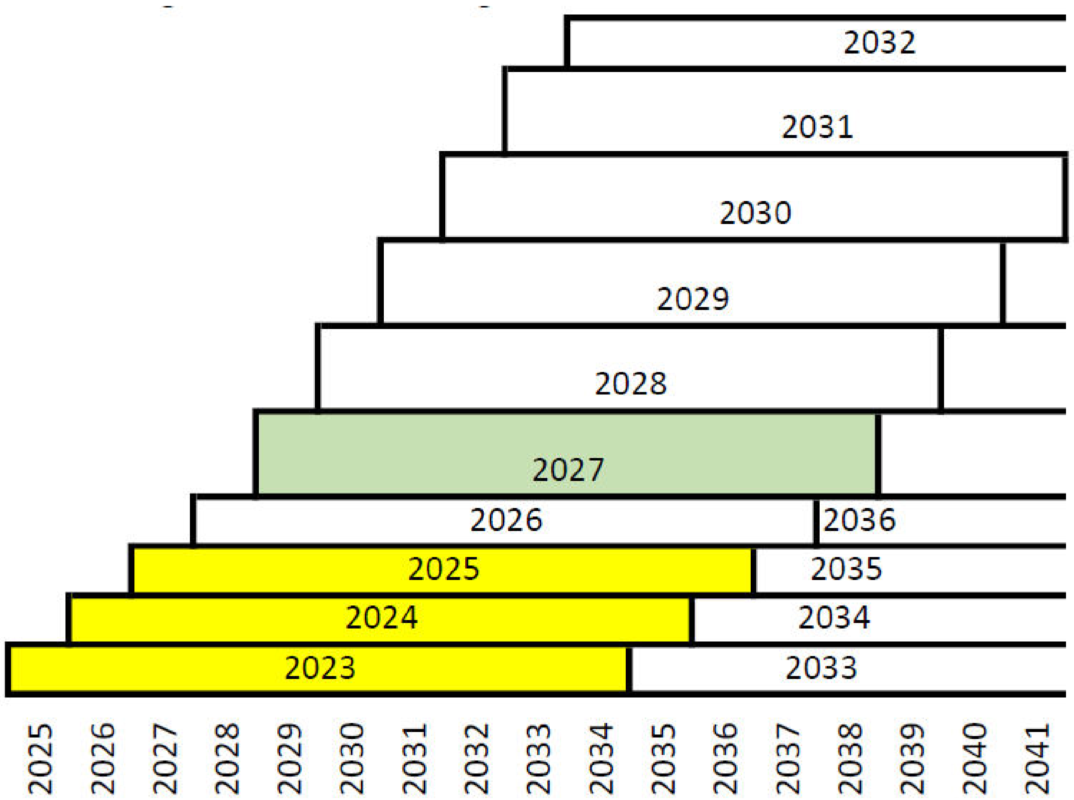


Advantages of „Future Quota“

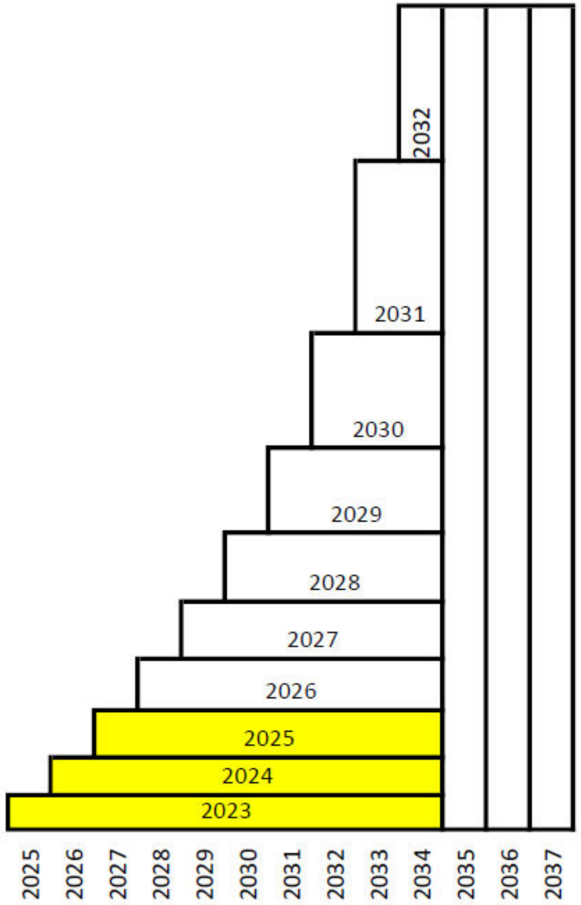
- Obligation can be implemented soon
- Obligation for a high overall percentage, even if annual contribution starts low
- Funding effect: Obligation year generally pays for investment and some part of expected operational deficit
- Low risks to investors from lack of follow-up quota and due to competition with new equipment with lower costs
- Change of policy possible
- **Larger immediate allocation effect**: The activity or consumption obliged by quota will be reduced by larger immediate price effect
- Few government activities (except by defining quote)

More options to design quota

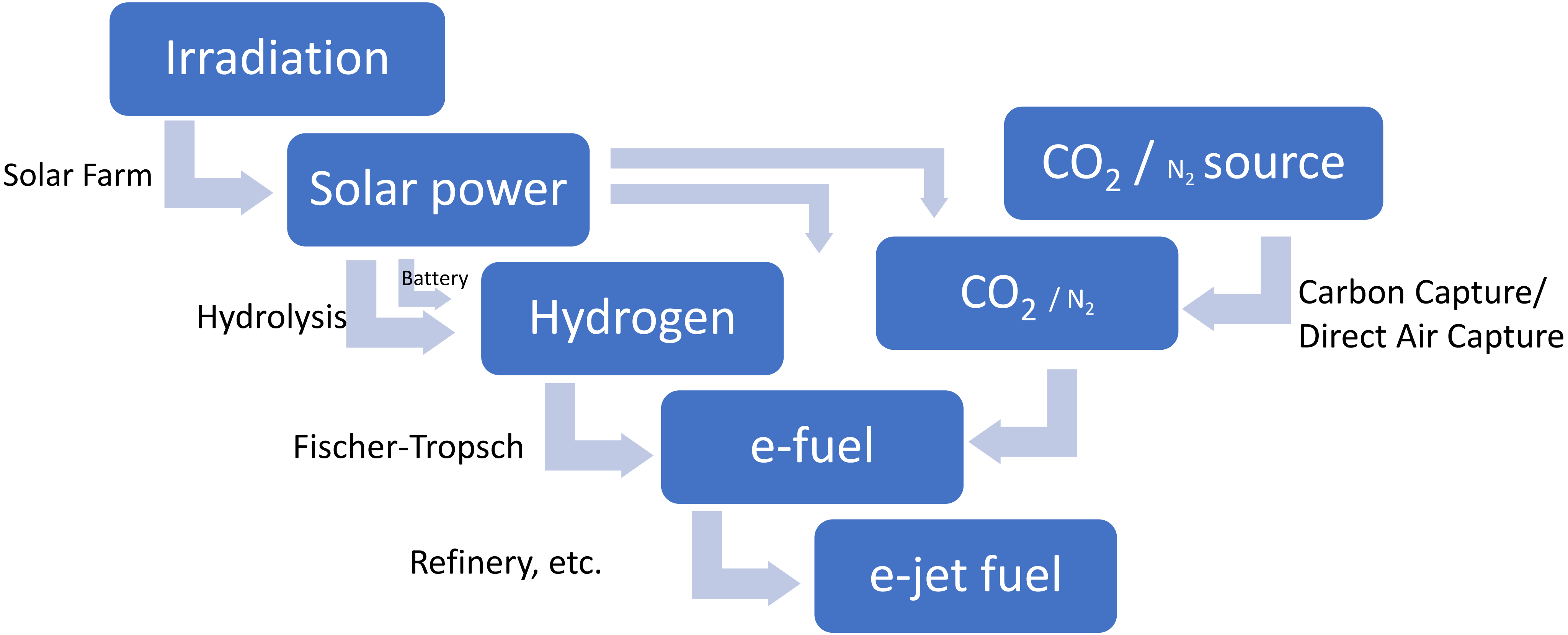
increasing quota



uniform end date



process steps to e-jet fuel



Irradiation

Solar Farm

Solar power

Battery

Hydrolysis

Hydrogen

CO_2 / N_2 source

CO_2 / N_2

Carbon Capture/
Direct Air Capture

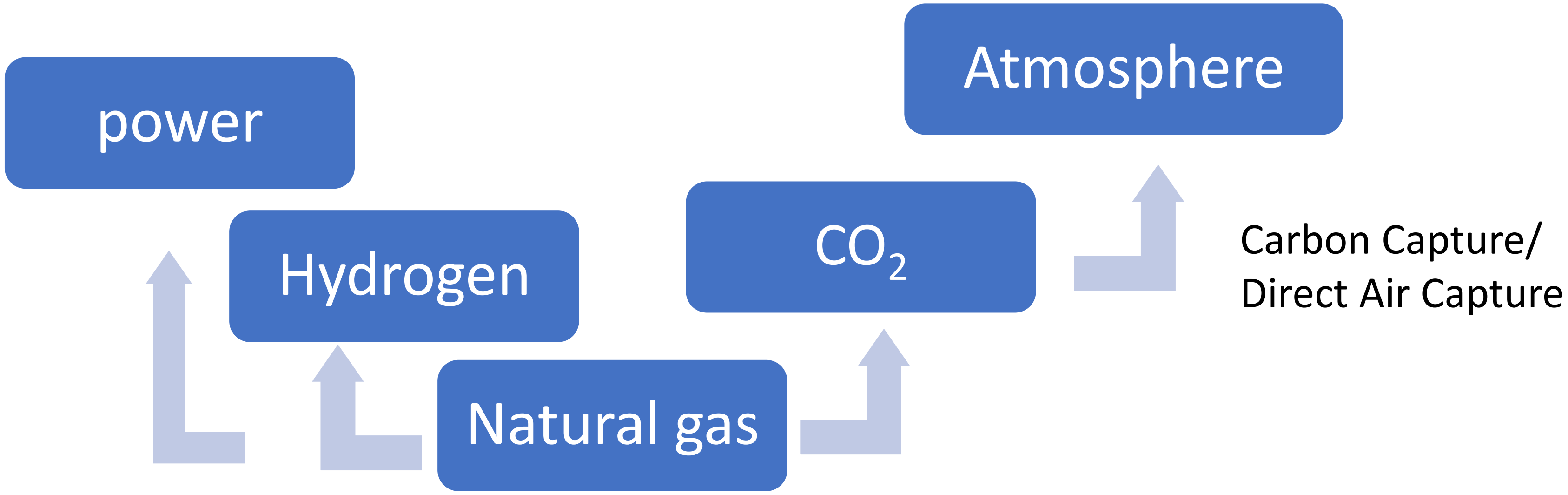
Fischer-Tropsch

e-fuel

Refinery, etc.

e-jet fuel

main procedures today



power

Hydrogen

Natural gas

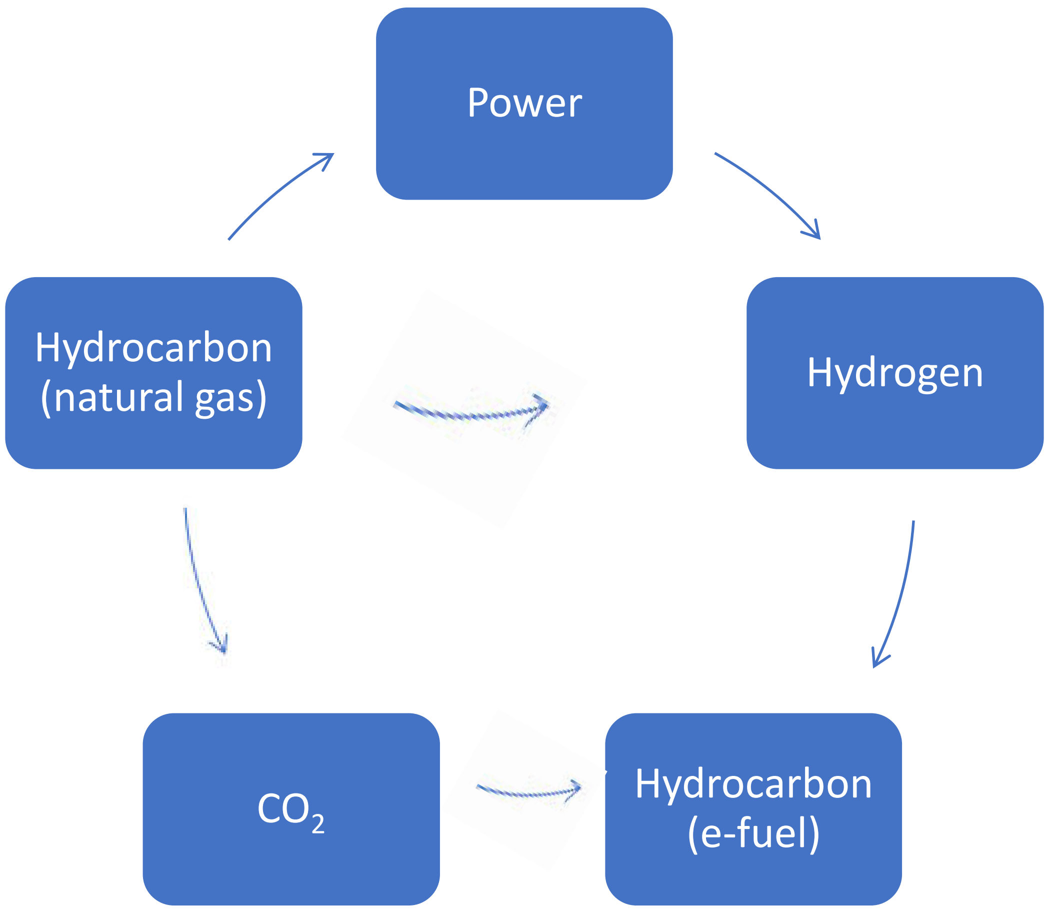
CO_2

Atmosphere

Carbon Capture/
Direct Air Capture

Avoid to perform opposite procedures at the same time

„Circular economy“ to avoid



Power

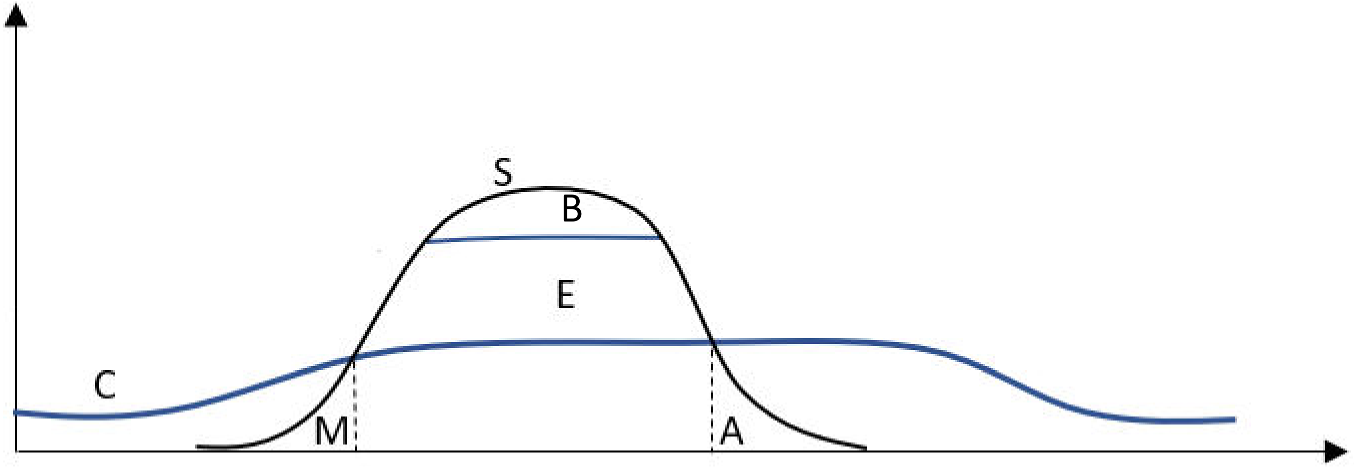
Hydrogen

Hydrocarbon (e-fuel)

CO_2

Hydrocarbon (natural gas)

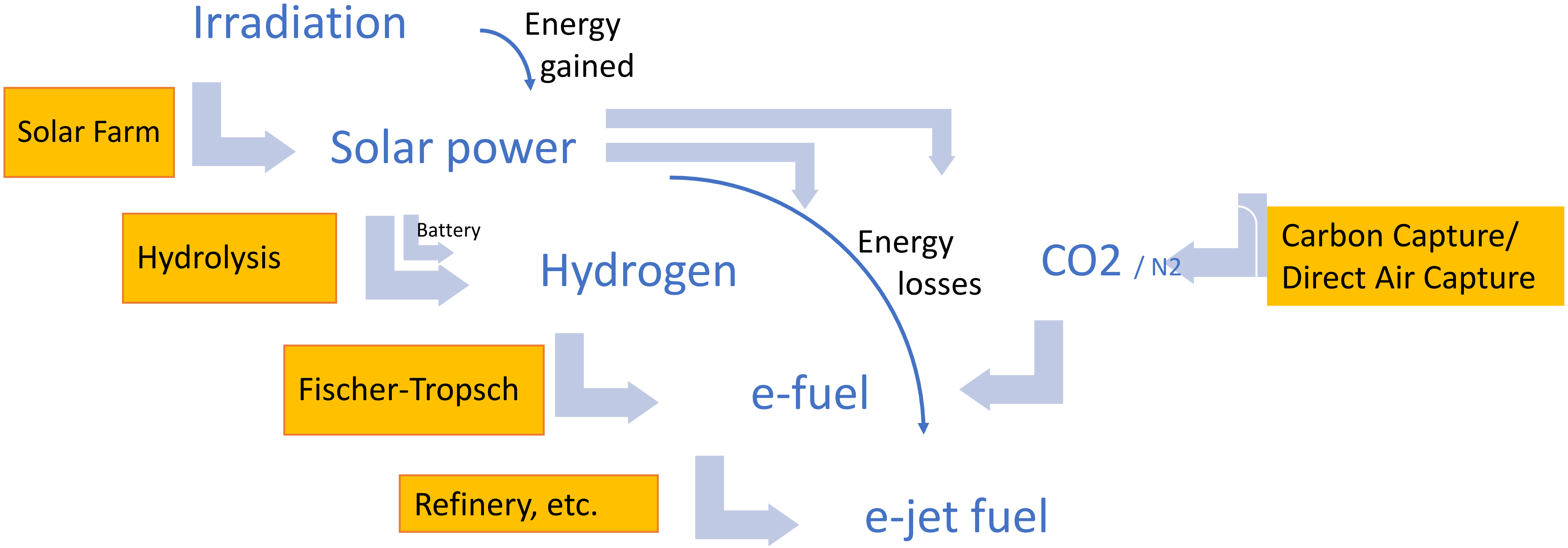
Power meaningfully used for electrolysis



C = Conventional power consumption during a day
S = Solar (or total of fluctuating renewable) power production ability
M, A = Morning and Afternoon when solar production is less than
conventional power consumption
E = power meaningfully used for electrolysis
B = curtailment of potential solar production, to avoid inadequate utilisation,
or used for battery storage

Maybe around one half of the solar power available can meaningfully be used for the power to gas process (electrolysis).

equipment to make e-jet fuel



Irradiation

Energy gained

Solar Farm

Solar power

Hydrolysis

Battery

Hydrogen

Energy losses

CO2 / N2

Carbon Capture/ Direct Air Capture

Fischer-Tropsch

e-fuel

Refinery, etc.

e-jet fuel

Costs of equipment to make e-jet fuel

These values shall just serve as example of order of magnitude and shall not be used as basis of further evaluations

	Invest	power out	full load hours	Years	annualised cost
Solar Farm	600 €/kW	150%	1000 (1/2 of 2000 h)	14	64 €/MWh
Hydrolysis	700 €/kW	100%	1000	14	42 €/MWh
Fischer-Tropsch	600 €/kW	t.b.d.	4000 (flexible re. power production)	14	11 €/MWh
Battery, Refinery, deduction for power sold etc.	to be determined		Total (estimate)		150 €/MWh
Carbon Capture / Direct Air Capture	To be determined (quite high for carbon capture?)			not included in total	

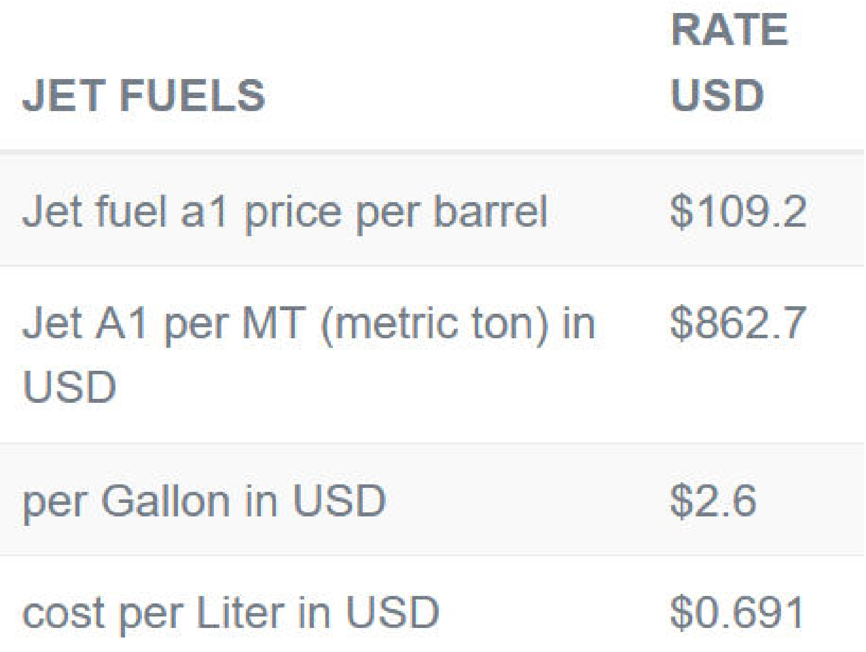
Price of jet fuel, travel and of 100% PtL-Quota

Price jet fuel	0,61 €/litre
Energy content	34.7 MJ/litre
Price per energy	0.0176 €/MJ
price per energy	63 €/MWh

Typ. fuel consumption

Lufthansa group 2019:	3,67 l / 100pkm
Frankfurt – Palma de Mallorca	1.265 km
fuel consumption	46 liter/pax
Energy content	0.45 MWh
* 150 €/MWh	67 €/pax

7 day package tour in season 1000 €/P typical



JET FUELS	RATE USD
Jet fuel a1 price per barrel	$109.2
Jet A1 per MT (metric ton) in USD	$862.7
per Gallon in USD	$2.6
cost per Liter in USD	$0.691

=> The investment costs from a 100% power-to-liquid quota, to be fulfilled over 14 years (7% annually), net of carbon capture, would lead to a moderate increase of travel costs (incl. accomodation)

jet-a1-fuel.com/price/germany, Luftlinie.org, tui.com (RIU hotels on Mallorca, half board, June 2022)
lufthansagroup.com/de/verantwortung/klima-umwelt/treibstoffverbrauch-und-emissionen.html

German coalition agreement for 2022-2025

- Wir unterstützen ambitionierte Quoten für Power-to-Liquid (PtL-Quoten) im Luft- und Schiffsverkehr, um einen Markthochlauf anzureizen.
- We support ambitious Power-to-Liquid (PtL) quotas in aviation and shipping to stimulate a market ramp-up.
- Wir werden ein Klimaschutzsofortprogramm mit allen notwendigen Gesetzen und Vorhaben bis Ende 2022 auf den Weg bringen und abschließen.
- We will launch and complete an immediate climate protection program with all the necessary laws and projects by the end of 2022.

- Go ahead with 100% PtL !

Question from discussion

Is a quota preferred over carbon pricing, and why?

Not generally, but carbon price may be set too low and will not promote new technologies with higher (initial) costs of carbon abatement, in particular in their early phase of implementation, like power-to-liquid processes. Therefore a combination of carbon pricing in segments with mature technology, which shall obtain broad implementation as soon as possible, and quotas in segments with still evolving technology may be more adequate. Also, carbon pricing will be less feasible in „international“ sectors like aviation and shipping. Finally, political support may be stronger for quotas compared to carbon pricing, also for the reason that they avoid „extra burden“ in the form of carbon prices being paid, but limit the costs to consumers to the cost of actual carbon abatement measures, in this case fulfillment of the quota.

DIFFER KIT Karlsruhe Institute of Technology vito Cerpotech HYGEAR INERATEC

KEROGREEN

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 Winter School

Future directions in research on Power-to-X for sustainable Chemicals & Fuels

10-11 February 2022

by Adelbert Goede, Project Coordinator

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

Acknowledgement KEROGREEN team

Michalis Tsampas[1], Richard van de Sanden[1], Stefan Welzel[1], Waldo Bongers[1], Ben Elzendoorn[1], Paola Diomede[1], Suleyman Er[1], Bram de Wolf[1], Floran Peters[1], Alex van de Steeg[1], Erik Langereis[1], Arunkumar Pandiyana[1], Vasileios Kyriakoua[1], Marieke van Ee[1], René Schoonen[1], Roland Dittmeyer[2], Peter Pfeiffer[2], Francisco de Sales Vidal Vazquez[2], Tabea Stadler[2], Michael Rubin (Klumpp)[2], Andreas Patyk[2], Manuel Andresh[2], Sabine Müller[2], Vesna Middelkoop[3], Marijke Jacobs[3], Anne Dalager Dyrly[4], Leonardo Roses[5], Ellart de Wit[5], Tim Böltken[6], Ricardo Jahns[6], Alexander Alekseev[7], Maarten van Dijk[8], Oskar Meyerink[8],

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 Technology and Services B.V
6. INERATEC, Innovative Chemical Reactor Technologies GmbH
7. LINDE AG
8. SkyNRG

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

Project Objectives

- End-to-end test of **integrated KEROGREEN process,** starting from recirculated CO_2 and H_2O to sustainable aviation fuel, powered by renewable electricity
- Research and optimization of individual process steps from TRL 1 – 3 to TRL 4
- Goal > 1L / day kerosene synthesis
- Project end date 30 Sept 2022

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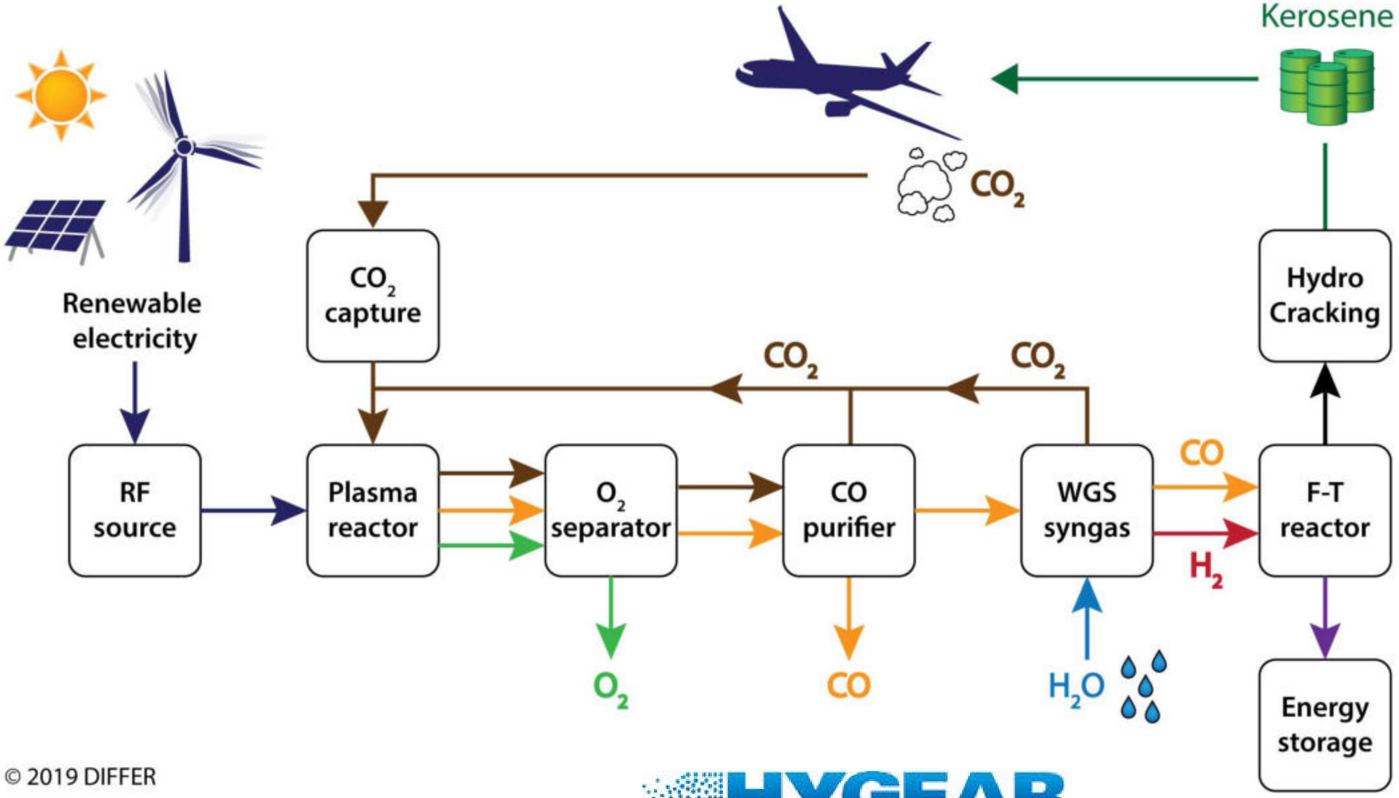
KEROGREEN Concept & Consortium



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HYGEAR

DIFFER

vito

KIT Karlsruhe Institute of Technology

INERATEC

Cerpotech

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Fuel Options for Sustainable Aviation

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

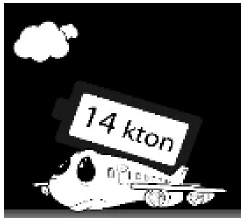
-> New aircraft design, fuel system, ground handling and storage system

Short haul flight may be -> 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**

Example: Airbus A 380 would need a 14.000 ton battery
to replace 260 ton kerosene pay-load in wings



Hybrid DLR H_2 Antares, 36 kW PEM Fuel Cell @ 80 kg,
10 kWh battery 45-60kW @ 50kg. **One seater** glider.
Range 750 km, speed 170 km/hr, altitude 4 km.
Why not use 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

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A third way: CO_2 Neutral Kerosene

Why CO_2 neutral synthetic kerosene?

- Climate Neutral fuel for **long haul transportation**
- employing **existing engine technology** and **infrastructure**
- Long term (seasonal), large scale (EJ) **energy storage** and **security**
- **Air Pollution; reduced emissions** No Sulphur, no soot, lower NO_x

What are the Challenges?

- Conversion of air (N_2, H_2O, CO_2,) into **energy dense fuels**
- **System Integration:** compact, decentralised, dynamic operation
- **Direct Air Capture** of **CO_2** to render the fuel cycle CO_2 neutral
- **P2X sector coupling** of renewable power to **fuel and chemical sector**

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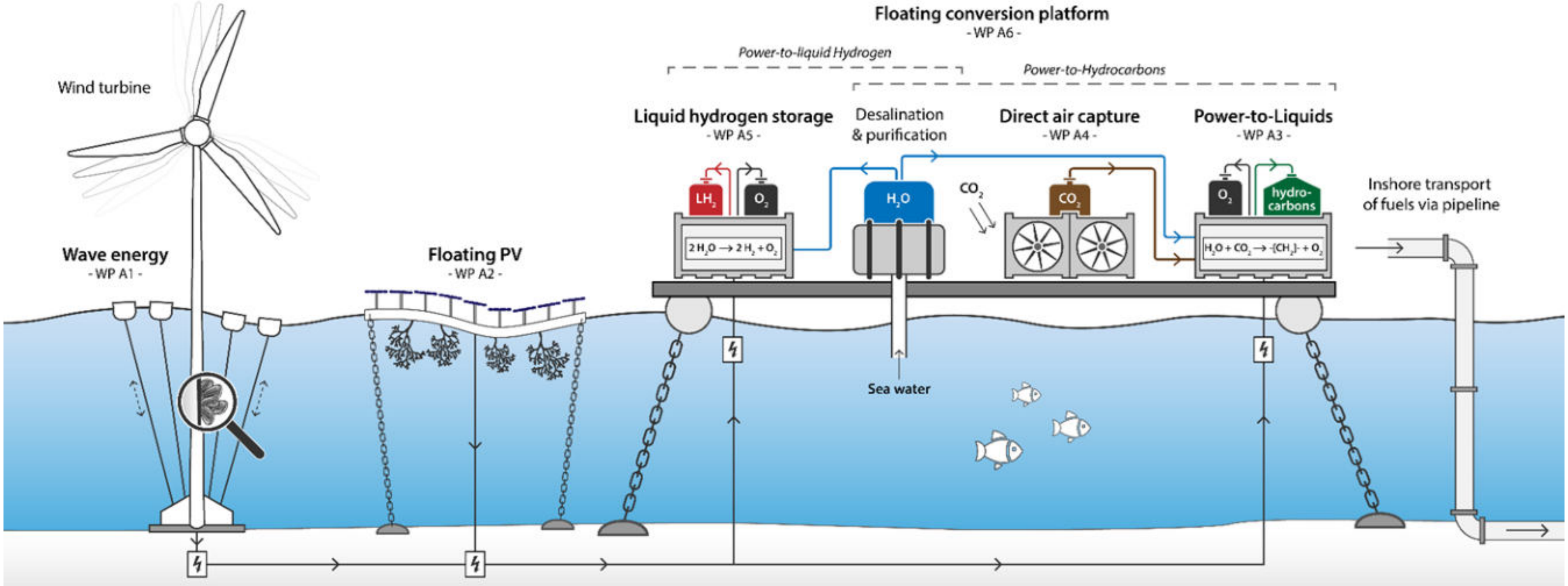
The ultimate goal?

Decentralised close-coupled P2X-DAC system



- **Sized to MW scale** of renewable electricity source
  (as opposed to GW chemical plants of today)
- **Close coupled** to renewable electricity source
  (transport of gas and oil is 20x cheaper than HV power lines)

KEROGREEN Winter School 10-11 February 2022
by Adelbert Goede

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

Main Results

- **Plasma reactor** for CO_2 splitting **operational** (DIFFER)
- **Oxygen separation** successfully **demonstrated** at lab scale (DIFFER).
- **Cell layer** deposition and characterisation at VITO.
- **Perovskite electrode** material produced by Cerpotech
- **Full scale Oxygen separator** prepared for **test at HyGear**
- **CO purifier commissioned** at HyGear
- Test **SE-WGS, FT and HC modules completed** at KIT
- **System Integration started** led by INERATEC
- Bulk of integration work scheduled for 2022 at KIT site

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CO_2 Reactor commissioned at DIFFER

DIFFER Team led by Stefan Welzel – Preliminary performance data!

Plasma reactor	$P_{RF\ 915\ MHz}$	CO_2 in [slm]	CO out	CO fraction
	6 kW	70	8.9-10.4	0.127-0.148
nominal	6 kW	50	9.3	0.186

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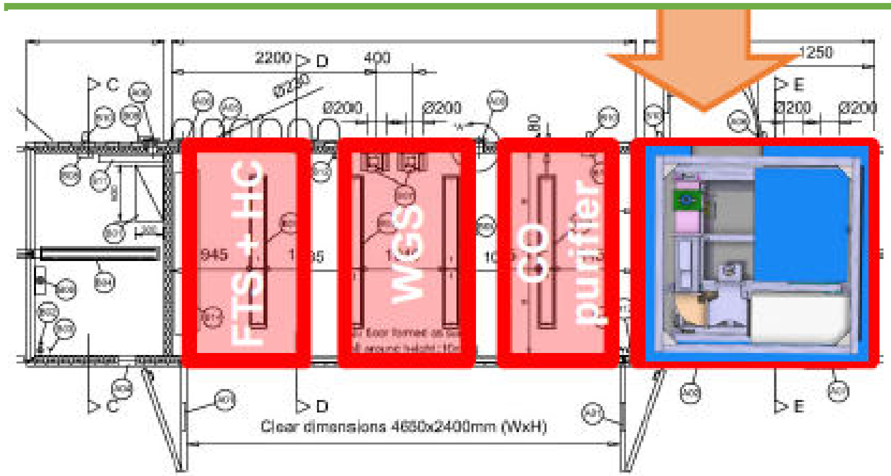
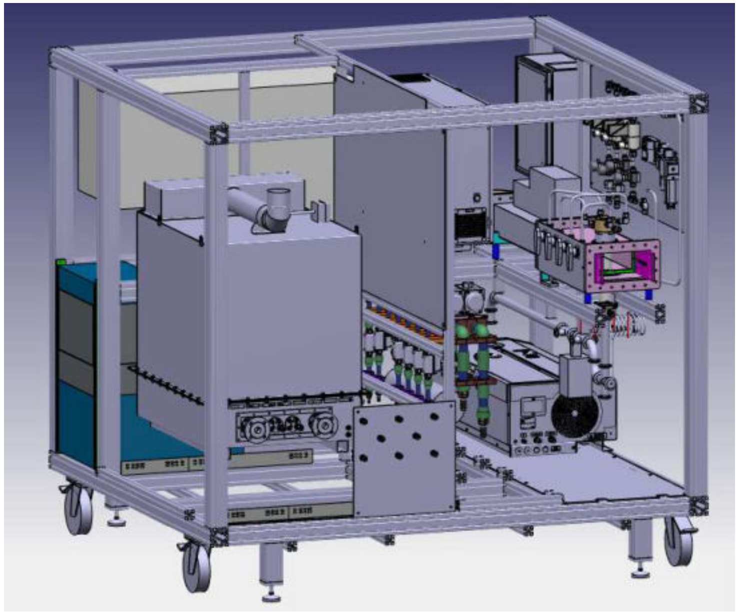
Plasma Reactor integration at DIFFER



KEROGREEN Plasma reactor integrated in container sized module



- Diffuse and high density contracted regime
- CO content scales with RF power in stochiometric ratio with O_2
- Energy efficiency and yield are inversely proportional
- Neutral gas temperature increases with power to over 5000K
- CO_2 Plasma dissociation theoretically explained by Luca Vialetto, including turbulent transport and ionic composition in diffuse and contracted regime

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

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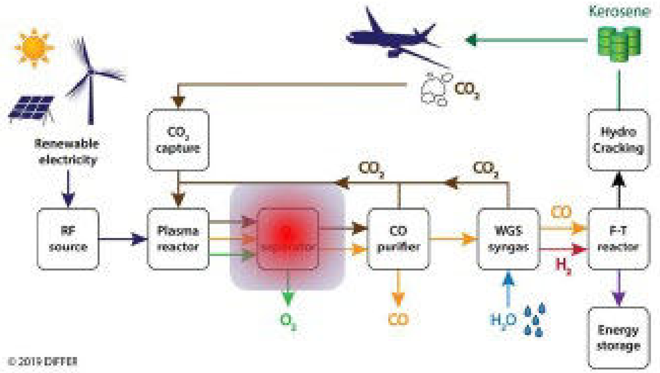
Major Challenge: Oxygen separation

Underlying research at DIFFER led by Mihalis Tsampas



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Results: Oxygen separation successfully demonstrated at DIFFER: product stream of integrated plasmolysis and electrochemical O_2 separation contains **91% less O_2 and 138% more CO** than plasmolysis alone. Unexpected **cell stability improvement** compared with electrolysis alone.

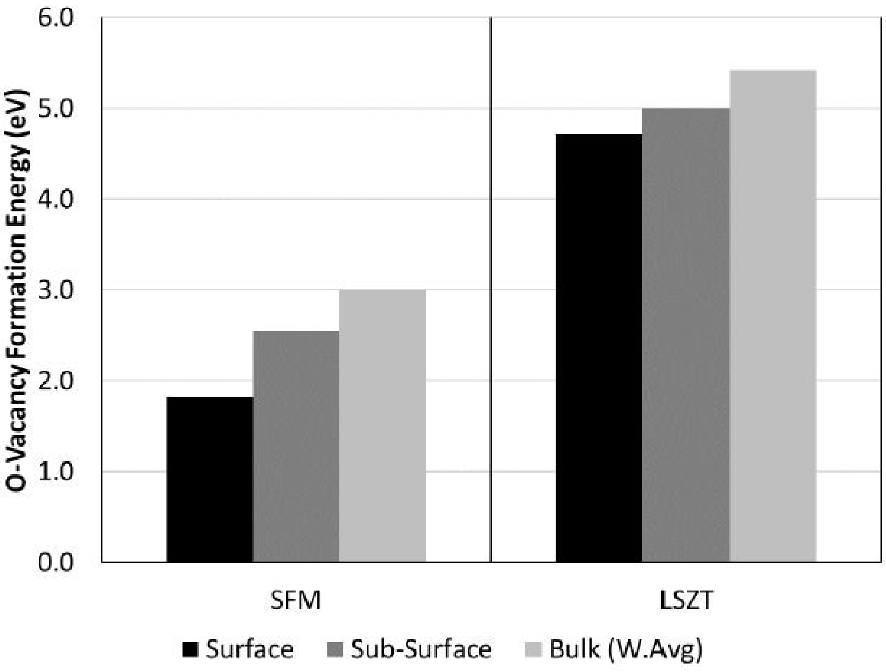
To be published: Journal of CO_2 Utilisation

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

Theory O_2 separation by DIFFER

Density Functional Theory (DFT) calculations by Suleyman Er (DIFFER)
Formation and Migration of Oxygen vacancies

- Oxygen vacancy created in bulk electrolyte
- Oxygen atoms from perovskite surface relocate to occupy bulk vacancies electrolyte
- O vacancy formation in SFM requires less energy than in LSZT
- But backreaction to CO_2 is less for LSZT
- **SFM selected for KEROGREEN**



Energy required to create an oxygen vacancy on the surface, sub-surface, and bulk layers of SFM and LSZT. The formation energies of O-vacancies are calculated as weighted average of all the O sites.

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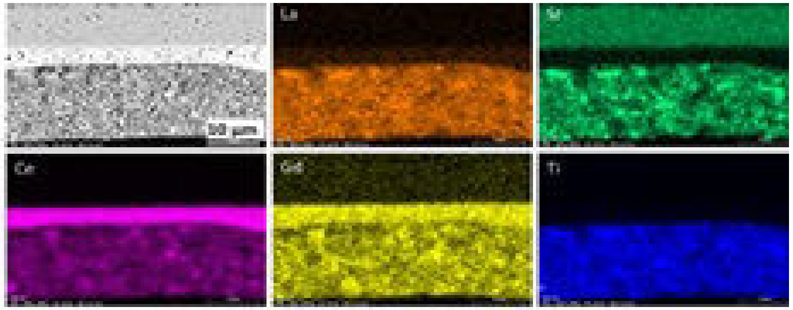
Cell layer material development at VITO

XRD of surfaces
SEM/EDS of surfaces and X-section

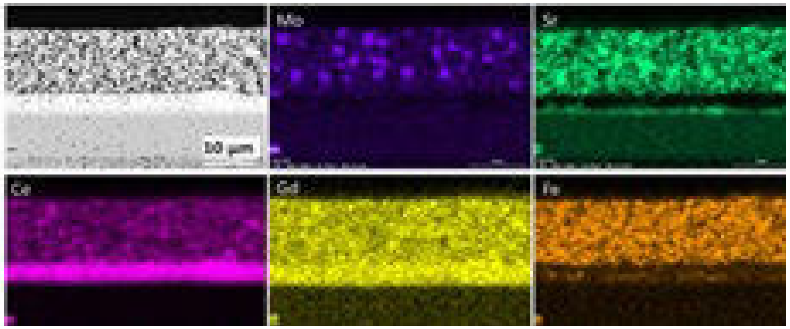
LSZT/GDC



Long-term exposure:

- LSZT/GDC stable
- SFM/GDC small changes

SFM/GDC



Spray coating technology
development to meet specifications
for uniformity, porosity and adhesion

Full scale cells obtained current densities under air at 700- 750 °C are close to the KEROGREEN targets i.e**. J = 0.25-0.30 A/cm^2**

Analysis of production costs and scale up of SOC based on full scale stack of 0.56 m^2 SOC SFM surface area for 0.1 kg kerosene/hr approx. 18k€/m^2

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

Oxygen Separator - Procurement

led by Stefan Welzel at DIFFER

Staged delivery:

- Powders supplied by Cerpotech (free issue item)
- Half cells and button cells for characterization
- 2 Small size stacks (500 cm^2), two types plasma electrode
- 1 Full size (5000 cm^2) Gas Separator

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

CO purifier by HyGear

Feed gas: CO/CO_2 mixture
Feed range: 15-90 slm
Feed Pressure: 0-200 mbar
Product pressure: 9 bar

CO yield after purification 78% at 98% purity

Preliminary performance data :
50 and 70 slm CO_2 input at plasma reactor.
Oxygen separation not included!

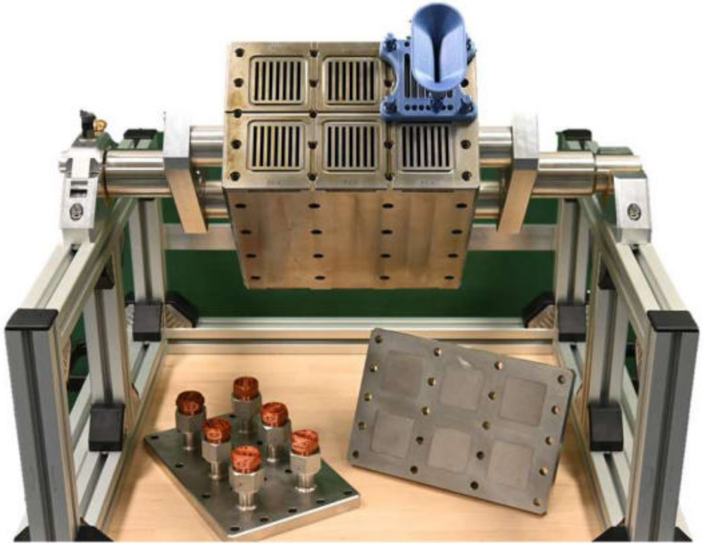
CO_2 in reactor	CO out reactor	Fraction CO PSA	PSA CO yield	CO out [slm] @ 98% pure
50 slm	9.3 slm	0.186	78%	0.78 x 0.186 x 50 = **7.25**
70 slm	10.4 slm	0.148		0.78 x 0.148 x 70 = **8.08**

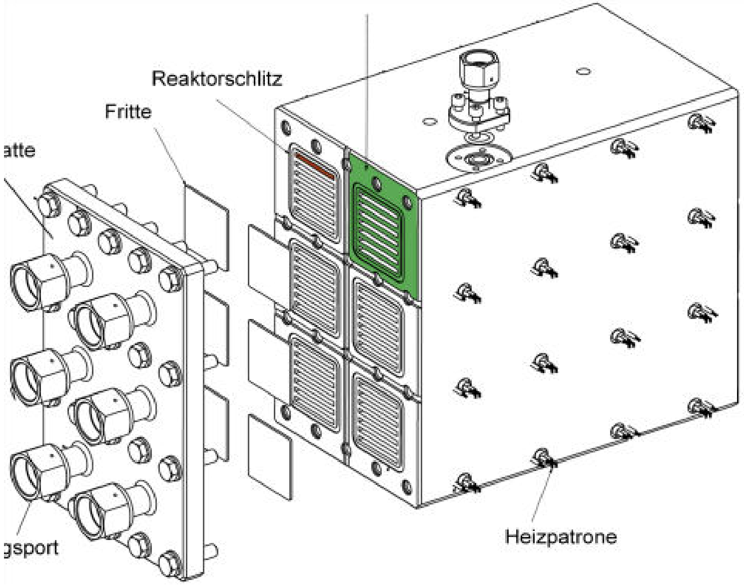
This project has received funding from the European Union‘s Horizon 2020 Research and Innovation Programme under Grant Agreement-Nr. 763909

Water Gas Shift reactor at KIT

Water Gas Shift reaction, enhanced by CO_2 sorbent and catalyst.

- Developed for **dynamic operation** enabling periodic switching between six reactive adsorption and regeneration channels
- **Dynamic modeling** for dynamic switching between absorption and regeneration channels to optimize H_2 yield
- Presently being **integrated** at the KEROGREEN pilot plant.





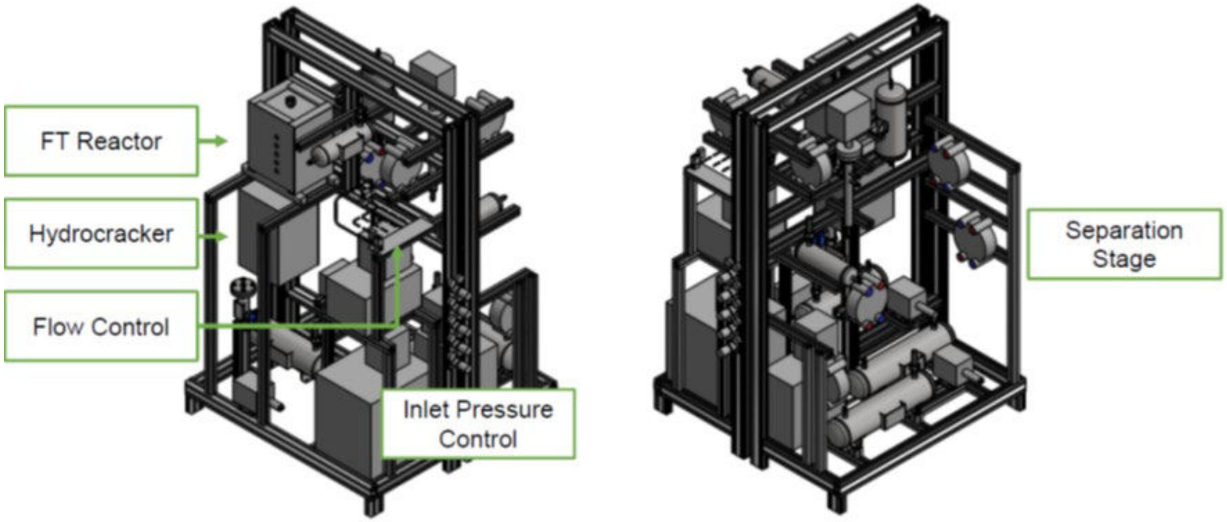
SEWGS module: Construction finalization, Testing, Commissioning

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

Fischer-Tropsch reactor INERATEC

Fischer-Tropsch reactor based on high heat transfer micro-structured reactor, with Co-based catalyst.

- **Compact and modular**. Upscaling through channel multiplication.
- **Heat** removal and **integration** at system level (SOEC heating)
- **3D printing** being pioneered at KIT



FT-HC reactor lay-out.

SE-WGS installed and tested

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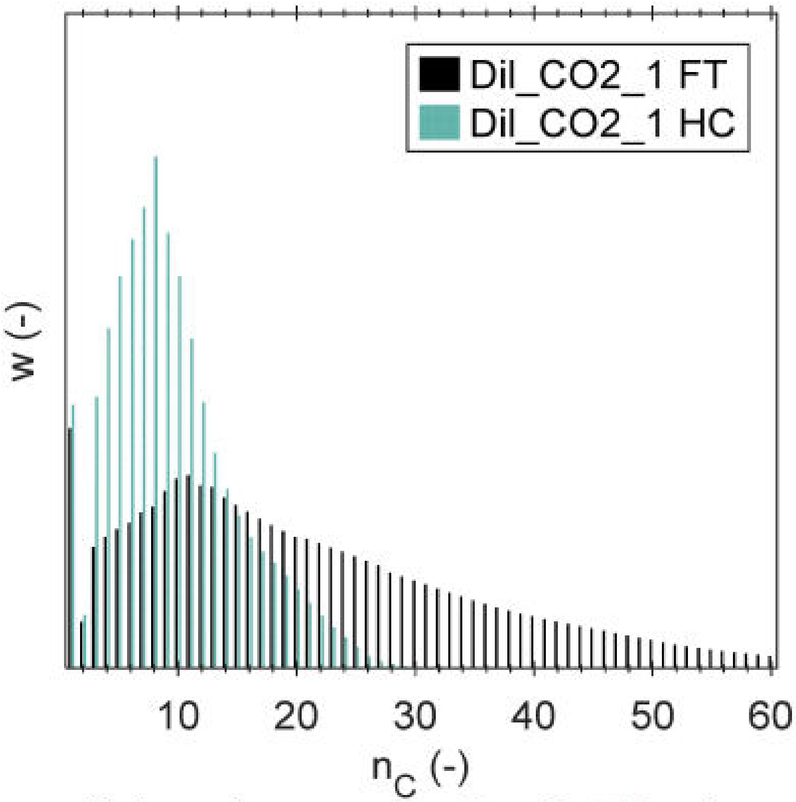
Hydro-Cracking reactor at KIT

Hydro-Cracking : hydration of the FT crude, isomerization to alkanes, no aromata, no alkenes.

- CO_2 acts as diluent with regard to reaction on the HC catalyst, needs to be improved
- C-distribution too wide
- Net production of hydrocarbons in HC strictly limited to C14
- Alcohols contained in the aqueous phase of the FT crude are drastically reduced
- Diluting effect of CO_2 has to be considered

Hydrocracker Installed and testing



Hydrocarbon mass fractions for FT and coupled FT-HC measurement. FT feed: 38.8 % H_2, 19.4 % CO, 38.8 % CO_2, 3.0 % N_2, $WHSV_{FT}$ = 4.5 h-1.

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

System modelling

System performance simulation by INERATEC and KIT

Implementation of detailed models for:

- Plasmolysis and oxygen separation (DIFFER)
- CO purification unit (HyGear).
- SE-WGS (KIT-IMVT)

Integrated system model to calculate CO_2 utilization and energy efficiencies

Simulation results are input to LCA studies by KIT-ITAS

*Overall system performance with **no** Oxygen extraction included in conversion shows ~1 slm kerosene fuel. Input O_2 data planned for March 2022*

CO_2 in reactor	CO 98% PSA out	CO:2H_2 WGS in	FT crude out	HC fuel out	Overall crude	HC fuel
50 slm	7.25 slm	0.3	0.92	0.5	7.25x0.3x0.92 = 2 slm	1 slm
70 slm	8.08	0.3	0.92	0.5	8.08x0.3x0.92 = 2.23 slm	1.11 slm

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

System Integration – led by INERATEC

KEROGREEN container sized plant at Karlsruhe Inst Technology

Integration KEROGREEN system started!

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

Sustainability assessment by KIT-ITAS

Development of material and energy flow and cost models

For more information attend PhD session Manuel Andresh Friday afternoon

Results

- **GWP reduction of at least 70%** possible with O_2 as by-product
- **Availability of plant** especially relevant for economic feasibility
- Higher price of offshore wind electricity evened out by higher availability in comparison to other electricity sources
- Utilization of electricity from photovoltaics for KEROGREEN in Germany not competitive in terms of GWP (greenhouse warming potential)
- **Assessment of alternative locations**, also for wind power

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

Expected Specific Impact

KEROGREEN produced CO_2 neutral kerosene
meets climate and environmental requirements of:

- UN-ICAO, EU Green Deal and COP-26 Glasgow 2021
- UN - CORSIA (Carbon Offsetting and Reduction Scheme for International Aviation) 2019
- EC-RTD-CETP-Clean Aviation (European Partnership under Horizon Europe) 2020

KEROGREEN Synthetic Fuel technology also **relevant for**

- Fuel for **shipping and long haul road transport**
- Long-term, Large-scale **Energy Storage**,
- **Grid stabilization** at increasing share of intermittent power

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

Summary of achievements

- CO_2 plasma reactor 6 kW commissioned for integration
- SOEC underlying research, development, procurement
- CO purification unit ready for integration
- Integration WGS-FT-HC module in hand
- Sustainability studies underway
- Project target 0.1 kg/hr kerosene within reach if oxygen can be successfully removed

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

DIFFER

Any Questions ?

DIFFER
Dutch Institute For Fundamental Energy Research
De Zaale 20, Eindhoven, the Netherlands
www.differ.nl

KEROGREEN

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

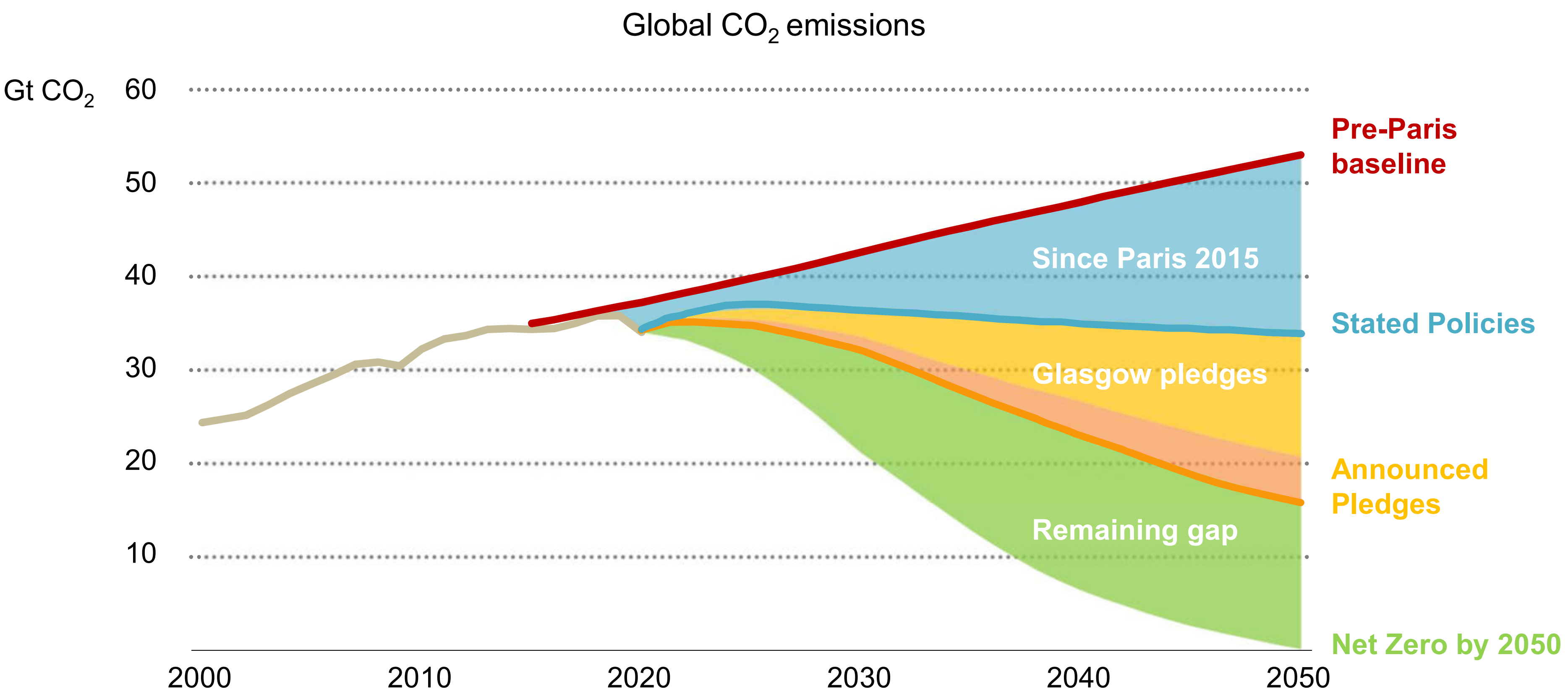
Hydrogen and the Net-Zero Emissions 2050 Scenario

Dr Ilkka Hannula – Senior Energy Analyst

11 Feb 2022

International
Energy Agency

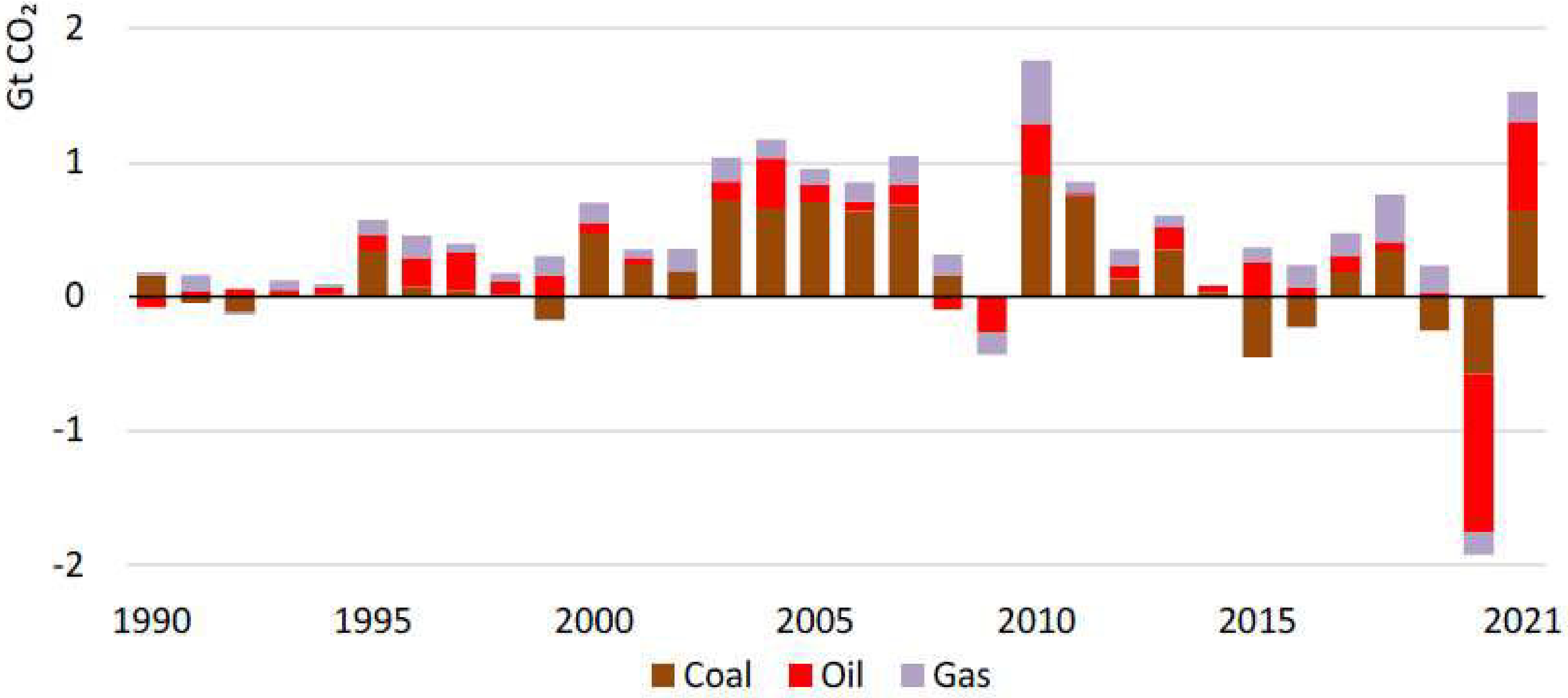
Where are we along the road to Net Zero by 2050?



For the first time, today's pledges – if implemented on time and in full – would keep the rise in global average temperatures in 2100 to below 2°C, but there's still a large gap to 1.5°C

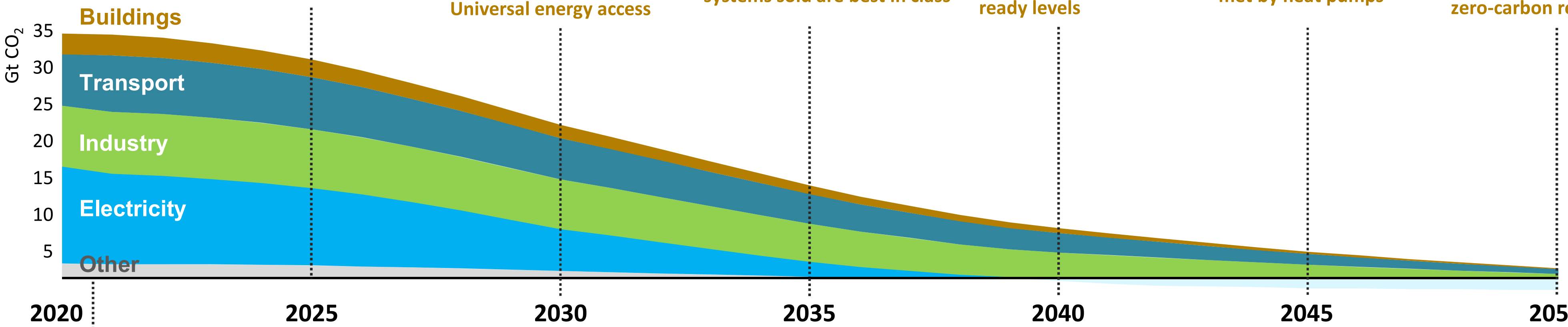
Targets alone are not enough

Change in global CO2 emissions by fuel, 1990-2021



After the largest ever decline due to the Covid-19 crisis, global CO2 emissions are set to increase by nearly 5% in 2021, approaching the 2019 peak, as demand for coal, oil & gas rebounds with the economy

Set near-term milestones to get on track for long-term targets



2020

No new unabated coal plants approved for development

No new oil and gas fields approved for development, and no new coal mines or mine extensions

2025

No new sales of fossil fuel boilers

2030

Most innovative low-emissions technologies in heavy industry demonstrated at scale

Electric cars are 60% of sales

All new buildings are zero-carbon ready

Universal energy access

1 020 GW annual solar and wind additions

Phase-out of unabated coal in advanced economies

150 Mt low-carbon hydrogen; 850 GW electrolysers

2035

All industrial electric motors sales are best in class

No new ICE car sales

50% of heavy truck sales are electric

Most appliances and cooling systems sold are best in class

Overall net zero electricity in advanced economies

4 Gt CO_2 captured

2040

Almost 90% of existing capacity in heavy industries reaches end of their investment cycle

50% of fuels used in aviation are sustainable

Half of existing buildings retrofitted to zero-carbon ready levels

Net zero electricity sector globally

Phase-out of all unabated coal and oil power plants

2045

Half of heating demand met by heat pumps

435 Mt low-carbon hydrogen; 3 000 GW electrolysers

2050

More than 90% of heavy industry production is low emissions

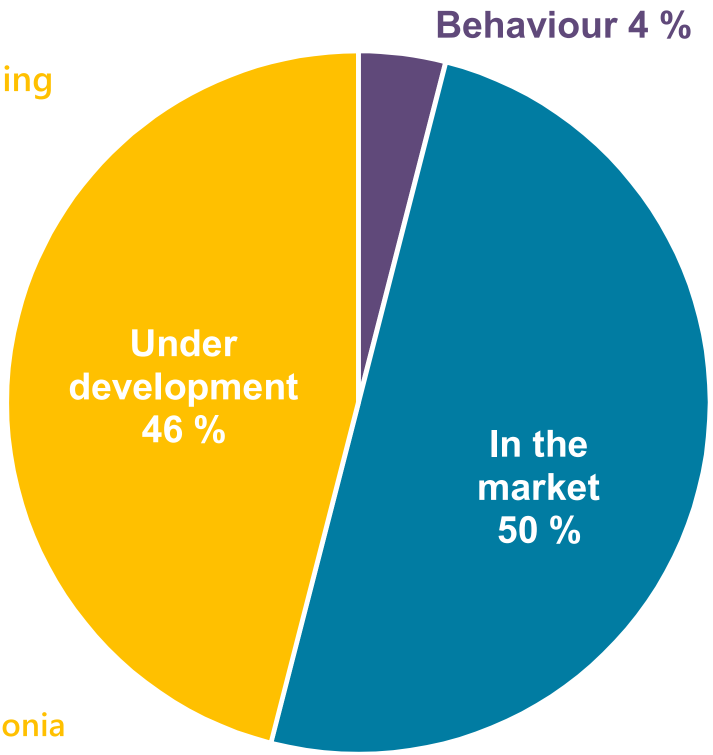
More than 85% of buildings are zero-carbon ready

Almost 70% of electricity generation globally from solar PV and wind

7.6 Gt CO_2 captured

Prepare for the next phase of the transition by boosting innovation

CO_2 savings by technology maturity in 2050, NZE scenario



Refrigerant-free advanced cooling

Advanced batteries

Next-generation biofuels

CO_2 capture from cement

Hydrogen-based steel

Small modular reactors

Synthetic liquid fuels

Electrolytic hydrogen for ammonia

Autonomous trucks

Optimised heat pump with storage

Direct air capture

Ammonia-powered ships

Electrolytic hydrogen for methanol

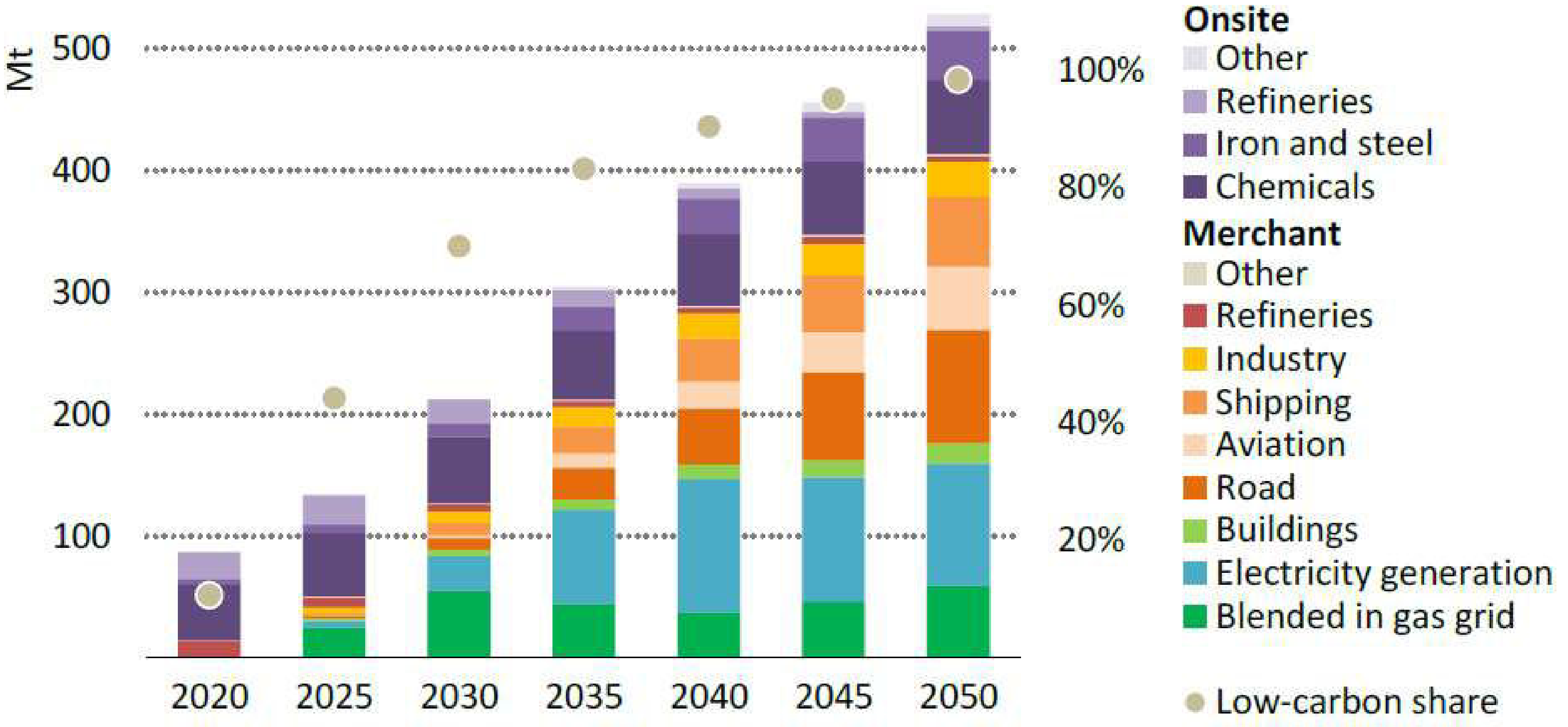
Building-integrated storage

Electric steam crackers

The oil and gas industry has a record of innovation that could help to unlock progress in sectors where emissions are hardest to abate

Use of low-carbon hydrogen expands rapidly in all sectors in the NZE

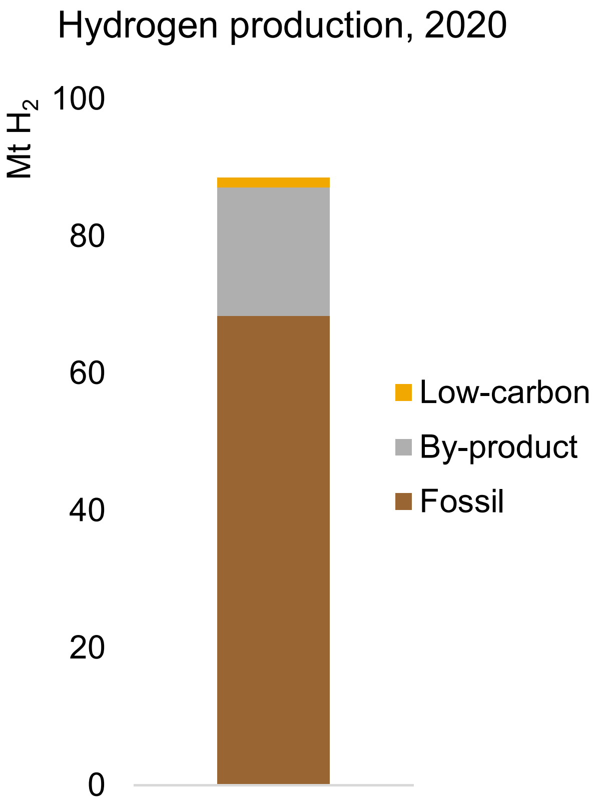
Global hydrogen and hydrogen-based fuel use in the NZE



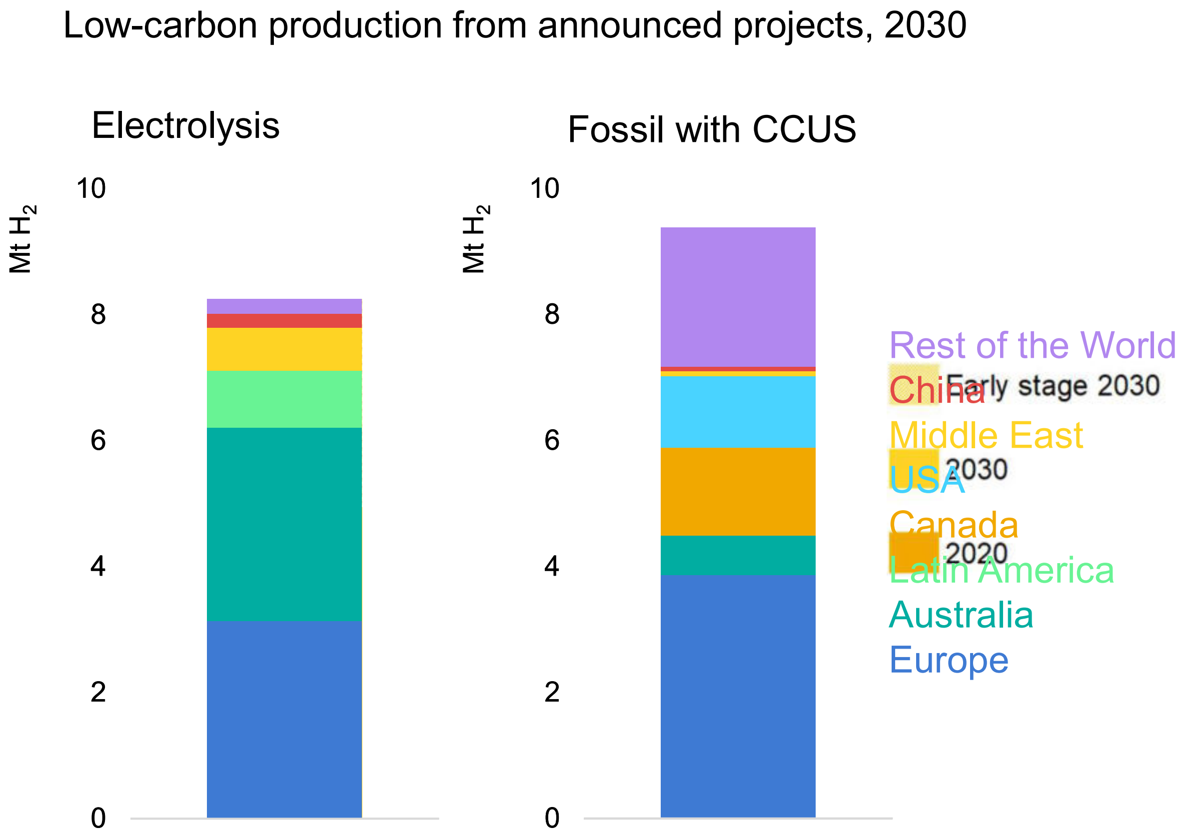
IEA. All rights reserved.

The initial focus for hydrogen is to convert existing uses to low-carbon hydrogen; hydrogen and hydrogen-based fuels then expand across all end-uses

The dawn of low-carbon hydrogen production



Hydrogen production, 2020

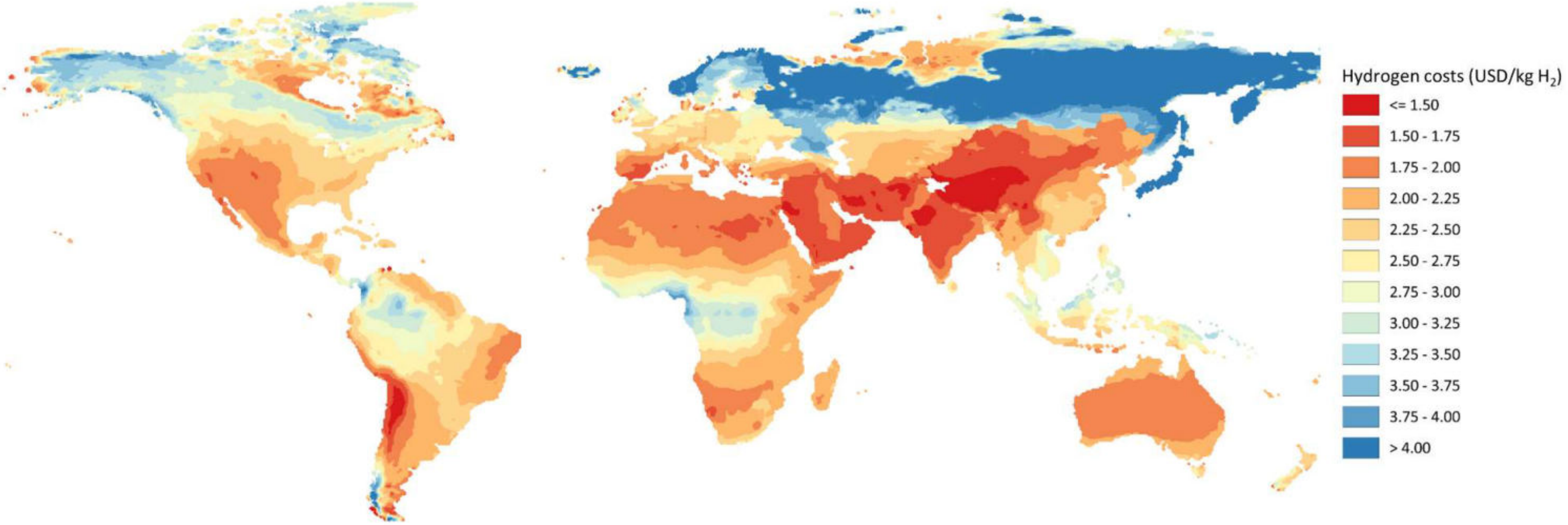


Low-carbon production from announced projects, 2030

Announced projects to produce low-carbon hydrogen are growing quickly, particularly in Europe, Australia, Canada, the United States and the Middle East. Around 17 Mt of low-carbon hydrogen could be produced by 2030

Low-carbon hydrogen costs are falling

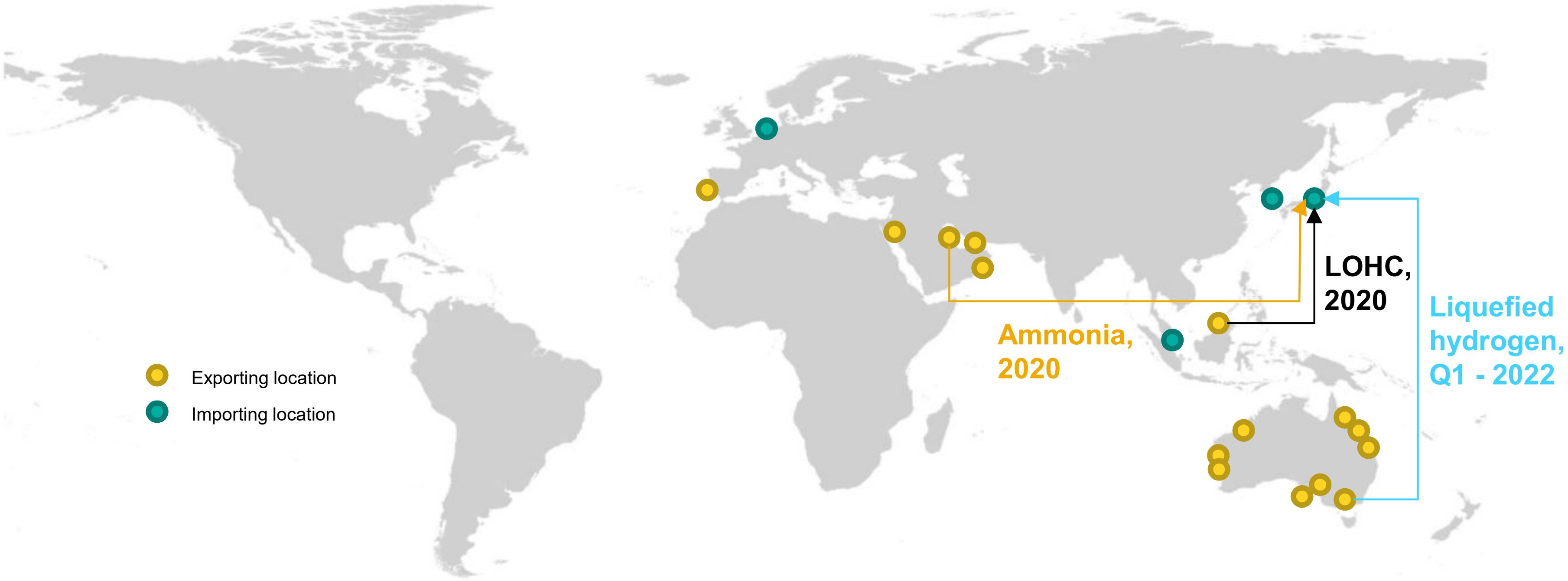
Hydrogen production cost from hybrid solar PV and wind systems in the NZE, 2030



Ambitious policy for deployment can make hydrogen from electrolysis competitive with hydrogen from fossil fuels within this decade

The first steps for international hydrogen trade have been taken

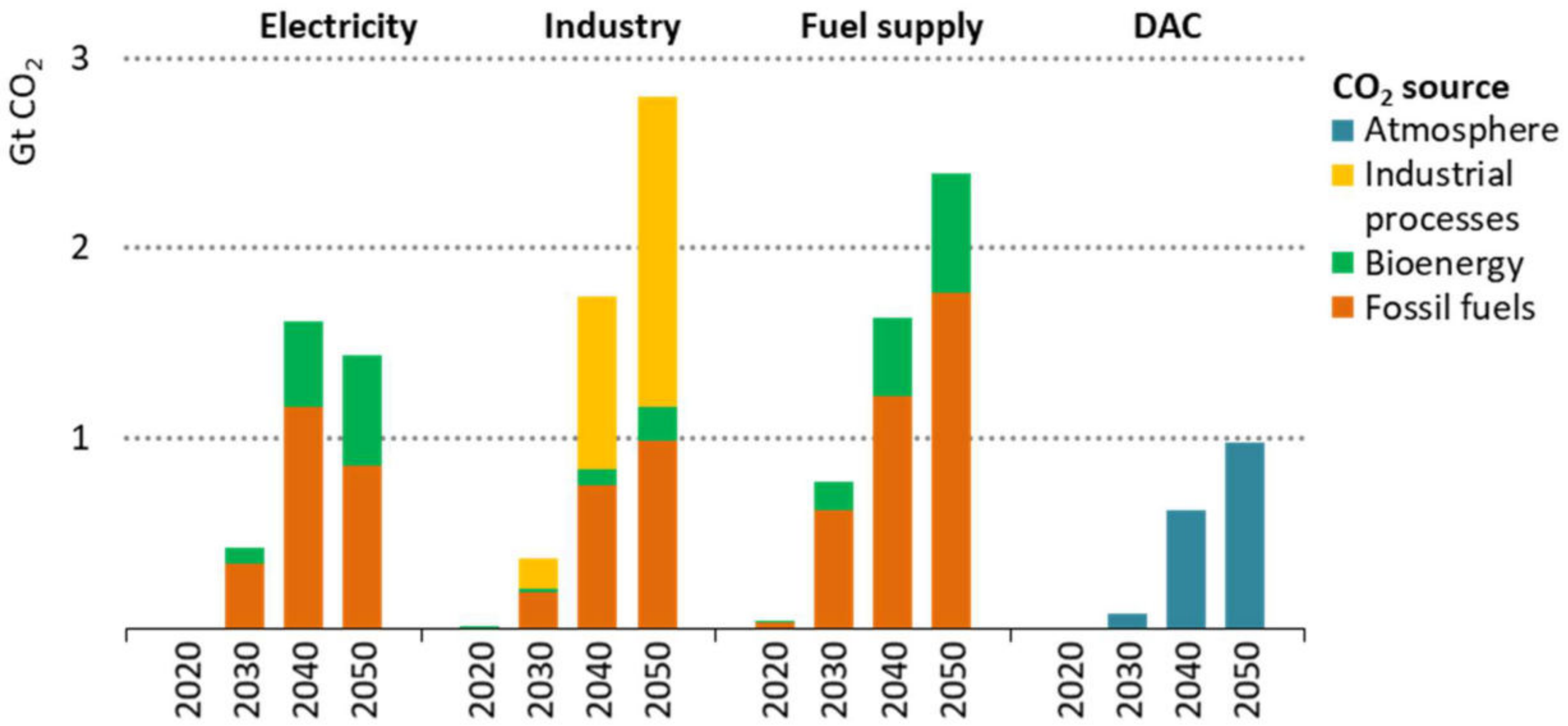
Selected international hydrogen trade projects



A global hydrogen market can help countries with limited domestic production potential and provide export opportunities for countries with good renewable resources or large CO_2 storage potential.

CCUS plays significant role in industry

CCUS by sector and emissions source in the NZE



By 2050, 7.6 Gt of CO2 is captured per year from a diverse range of sources.
A total of 2.4 Gt CO2 is captured through BECCS and DACCS, of which 1.9 Gt CO2 is permanently stored.

From momentum to implementation

- Hydrogen had many false starts but there are strong signals for the energy sector that this time could be different – momentum is turning into action:
    - A growing number of governments is defining the role of hydrogen in their energy strategies
    - Industry is moving to seize the opportunity and is increasing hydrogen-related investments
    - International cooperation has taken centre stage
- Many factors are at play that may explain the momentum; efforts to mitigate climate change and the growing number of net zero commitments are important factors
- The future for hydrogen looks bright but whether on-the-ground progress is fast enough and going in the direction required for hydrogen to play its part in addressing climate change is a key question

DTU

Peter Holtappels

Kerogreen Winterschool 2022

Organic Electrosynthesis: a sustainable route to polymers and other high value chemicals?

Peter Holtappels, DTU Energy, peho@dtu.dk

With contribution from:

- Christos Chatzichristodoulou
- Khurram S.Joya
- Marie Lund Traulsen
- Florian Gellrich
- Mathias Christensen

2015 -2019 EU Grant Agreement 677471

- David Tran

OrganicES
2022-2025

INDEPENDENT RESEARCH FUND DENMARK

Brief historical overview: Organic ElectroSynthesis

- **Faraday 1834**: to demonstrate the validity of his Faraday constant (Q= nNF)
  - C_2H_6 formation from $NaCH_3COO$ → reduction of carboxylic acid group
- **Kolbe reaction 1849** -54: Alkane synthesis from fatty acids
  - $R\text{-}COO^- + R\text{-}COO^- \rightarrow R\text{-}R + 2\ CO_2 + 2\ e^-$
  - Industrially important process until 1980th

- **Bayer 1890**:
  - Synthesis of Anilin and phenylhydroxylamin synthesis

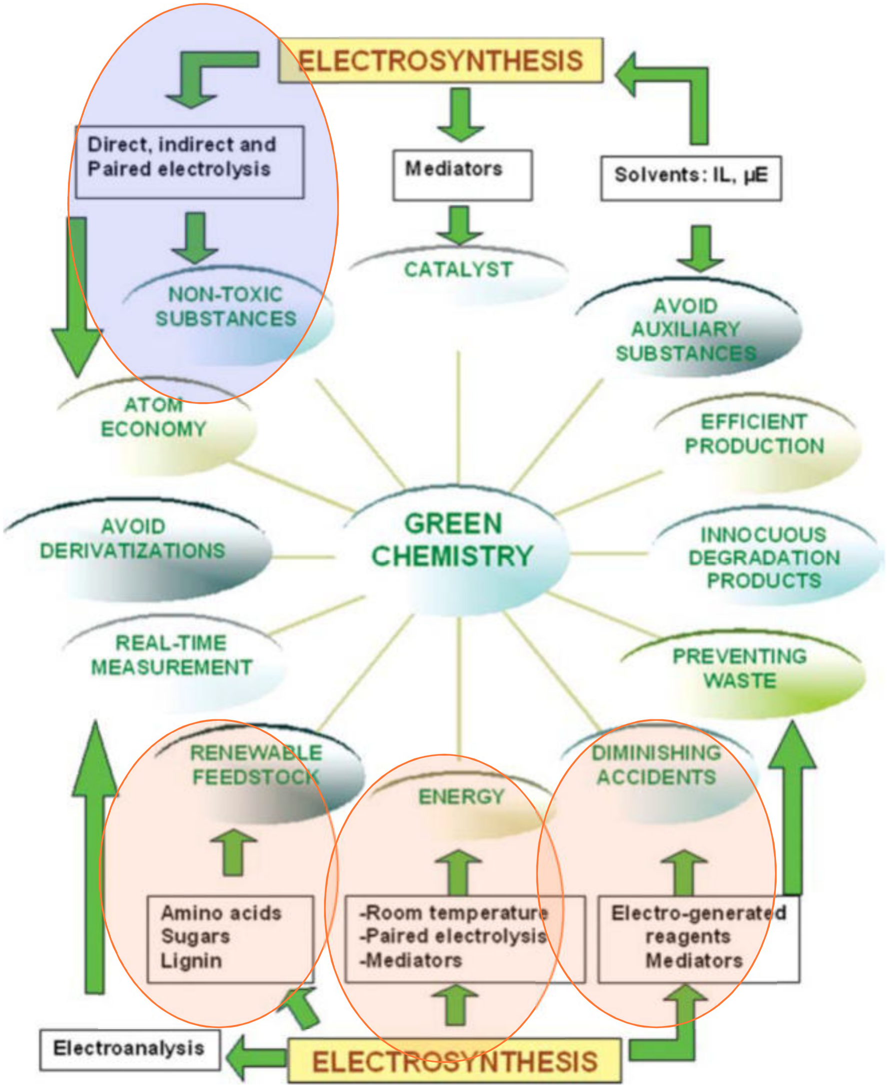
- **Baizer** / Monsanto **1960**:
  - Nylonfibre production (from acetonitrile by electrohydrodimerization)
  - Industrially important process until 1980th

Green Chemistry

- Integration of renewable electricity into chemical processes
- Utilization of “green” electrons as reactants

- Process intensification through paired reactions
  - – Tandemreactors

- Hydorgenation
- De-hydrogenation
- Oxidation
  - – Potential to omit OER



Fontana-Uribe et al. Green Chem., 2010, **12**, 2099–2119

Valuable building blocks from biomass

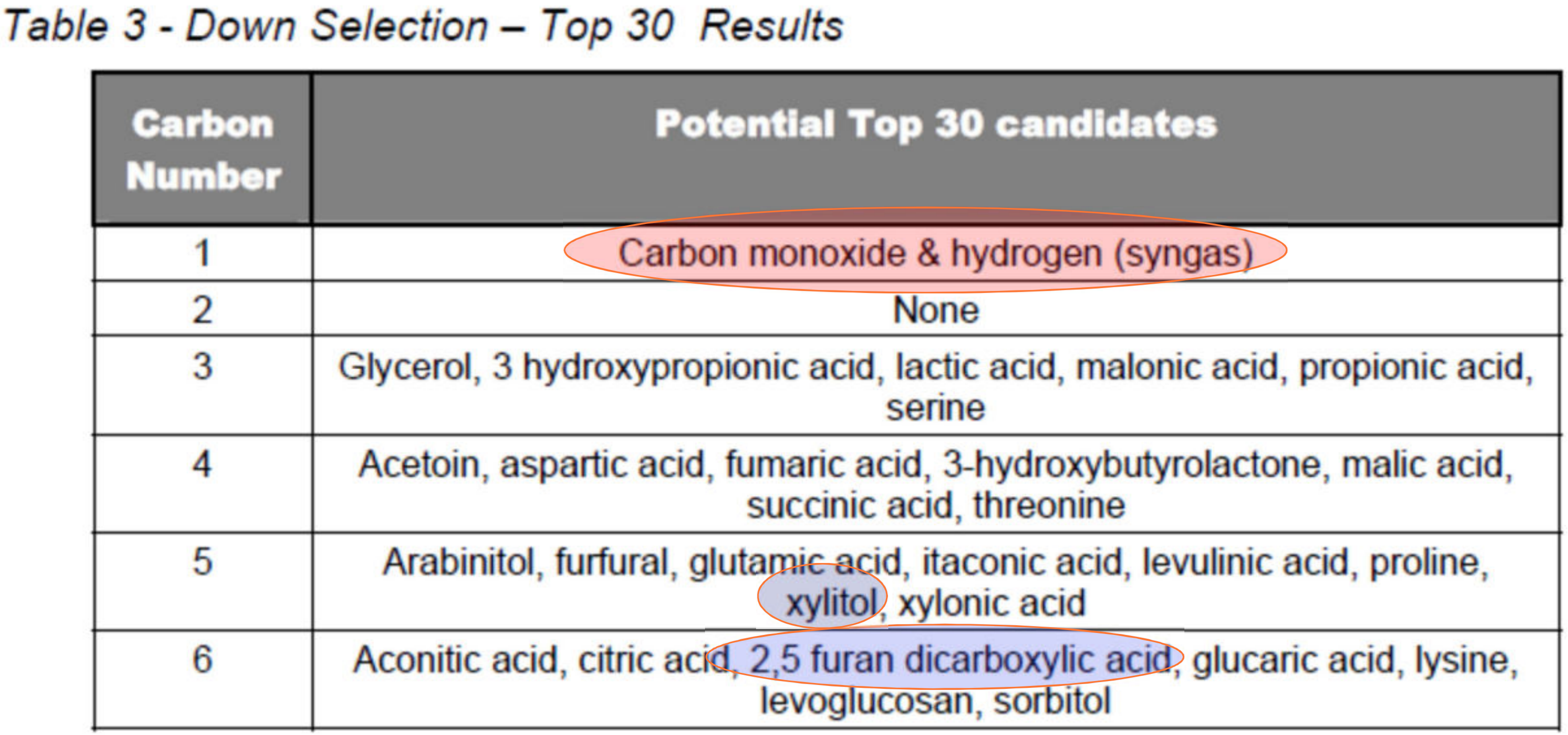


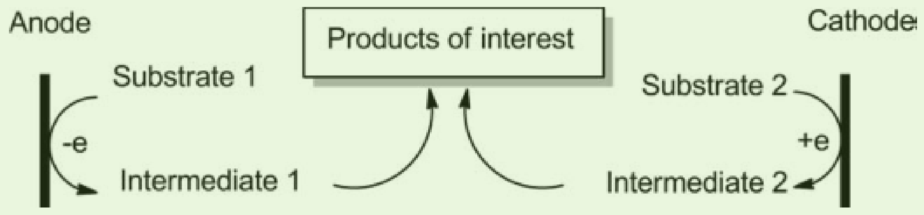
Table 3 - Down Selection – Top 30 Results

Carbon Number	Potential Top 30 candidates
1	Carbon monoxide & hydrogen (syngas)
2	None
3	Glycerol, 3 hydroxypropionic acid, lactic acid, malonic acid, propionic acid, serine
4	Acetoin, aspartic acid, fumaric acid, 3-hydroxybutyrolactone, malic acid, succinic acid, threonine
5	Arabinitol, furfural, glutamic acid, itaconic acid, levulinic acid, proline, xylitol, xylonic acid
6	Aconitic acid, citric acid, 2,5 furan dicarboxylic acid, glucaric acid, lysine, levoglucosan, sorbitol

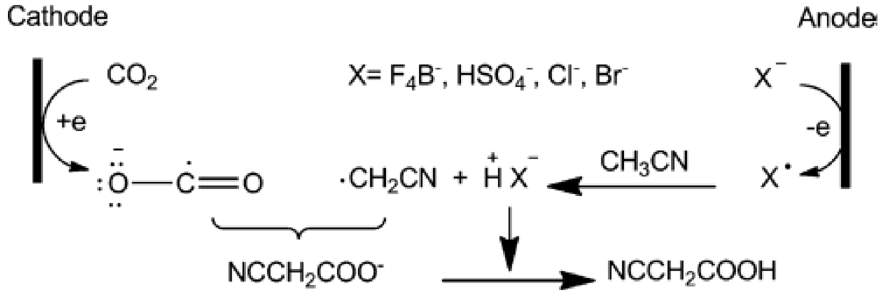
Werpy T., Petersen G., *Top Value Added Chemicals from Biomass, Volume 1 Results of screening for Potential Candidates from Sugar and Synthesis Gas*, **2004** Pacific Northwest National Laboratory, National Renewable Energy Laboratory, http://www1.eere.energy.gov/biomass/pdfs/35523.pdf

Paired electrochemical reactions

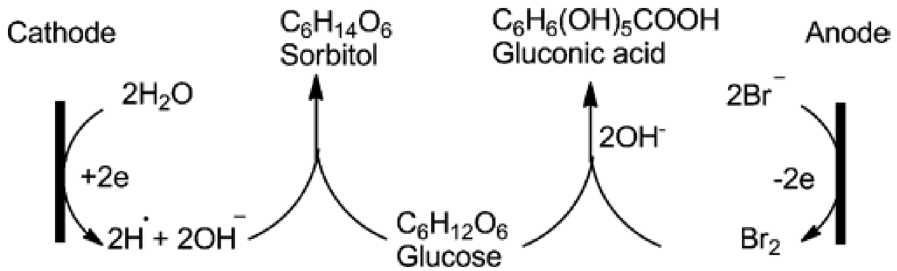
- Parallel
  - Both electrode processes produce a desired species



- Convergent
  - The products react to one final product



- Divergent
  - One educt reacts at both electrodes



- Linear
  - One substrate into one product (e.g. involcing redox mediators)

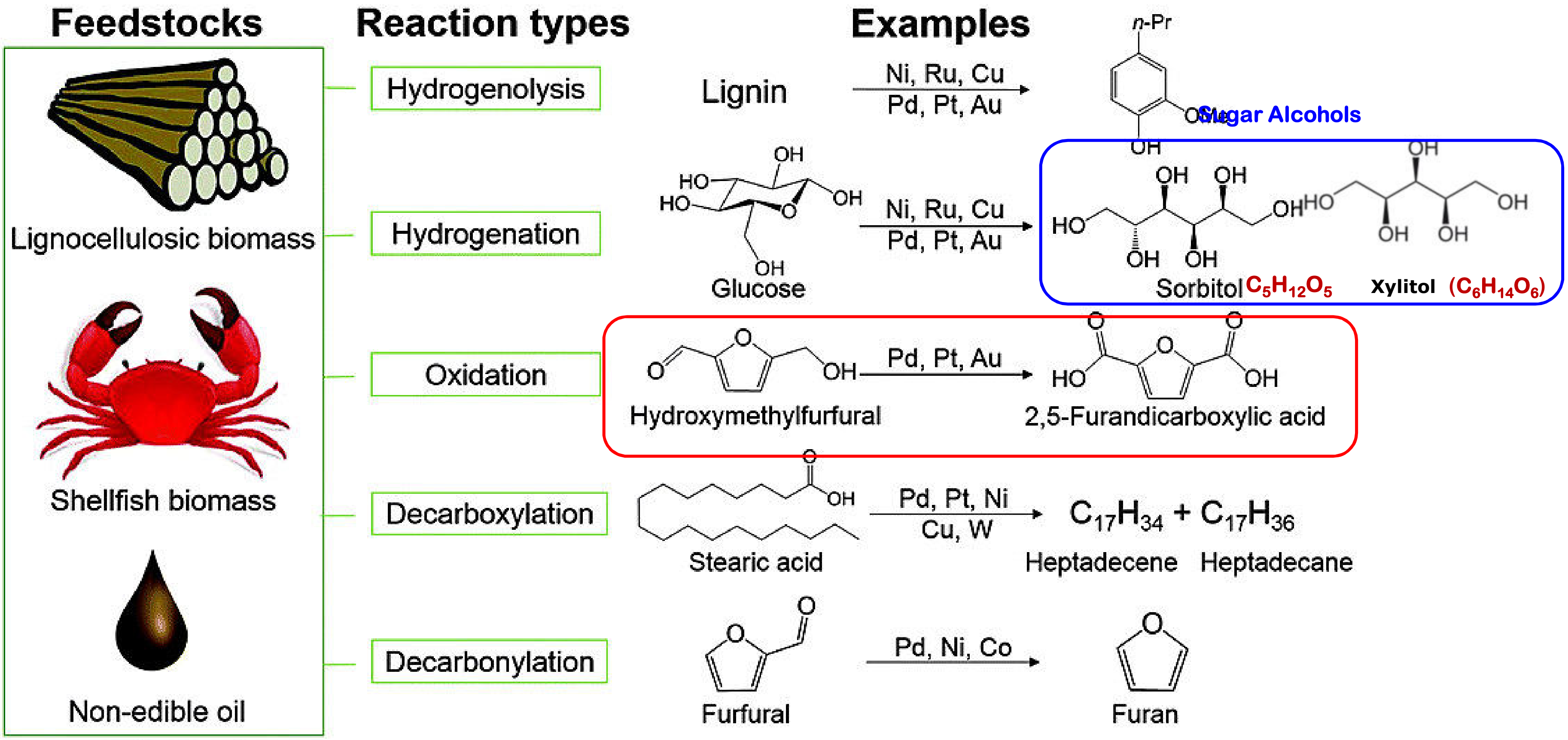
Fontana-Uribe et al. Green Chem., 2010, **12**, 2099–2119

❑ BIOMASS Electrolysis to Chemicals & Polymers

TERRA

Opportunities: Biomass Conversion

Biomass



Feedstocks

- Lignocellulosic biomass
- Shellfish biomass
- Non-edible oil

Reaction types

- Hydrogenolysis
- Hydrogenation
- Oxidation
- Decarboxylation
- Decarbonylation

Examples

Lignin → (Ni, Ru, Cu / Pd, Pt, Au)

Glucose → (Ni, Ru, Cu / Pd, Pt, Au) Sugar Alcohols: Sorbitol $C_5H_{12}O_5$ Xylitol $(C_6H_{14}O_6)$

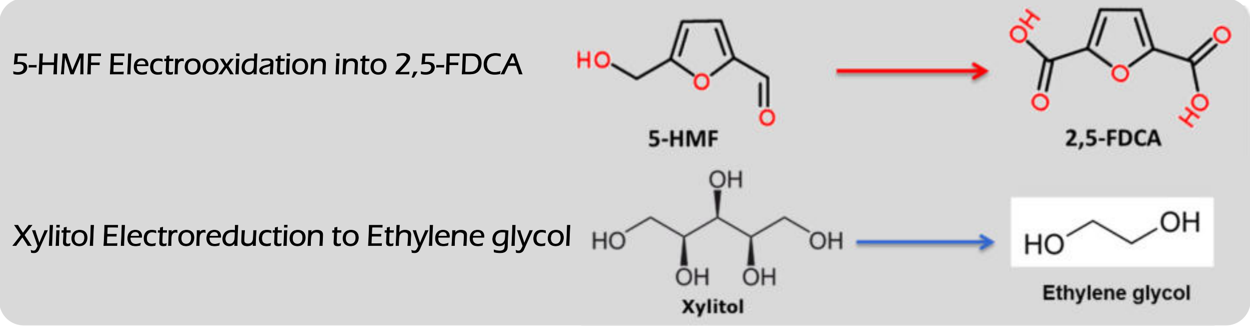
Hydroxymethylfurfural → (Pd, Pt, Au) 2,5-Furandicarboxylic acid

Stearic acid → (Pd, Pt, Ni / Cu, W) $C_{17}H_{34}$ + $C_{17}H_{36}$ Heptadecene Heptadecane

Furfural → (Pd, Ni, Co) Furan

❑ BIOMASS Electrolysis to Chemicals & Polymers

Why Biomass Conversion



5-HMF Electrooxidation into 2,5-FDCA

Xylitol Electroreduction to Ethylene glycol

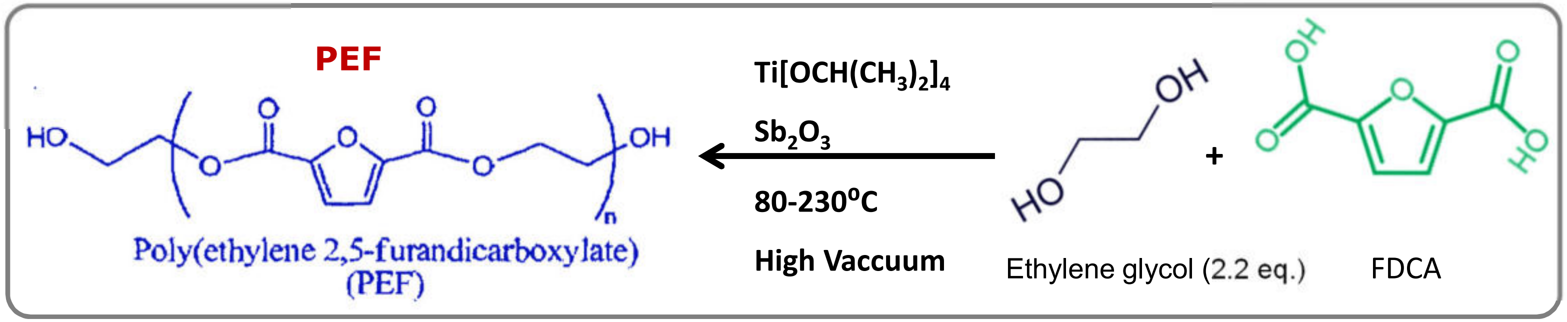
PEF (Polyethylene Furanoate)

will potentially replace the PET (Polyethylene terephthalate)

100% Natural

100% Recyclable polymer-plastic

Bio-degradeable



PEF

$Ti[OCH(CH_3)_2]_4$

Sb_2O_3

80-230°C

High Vaccuum

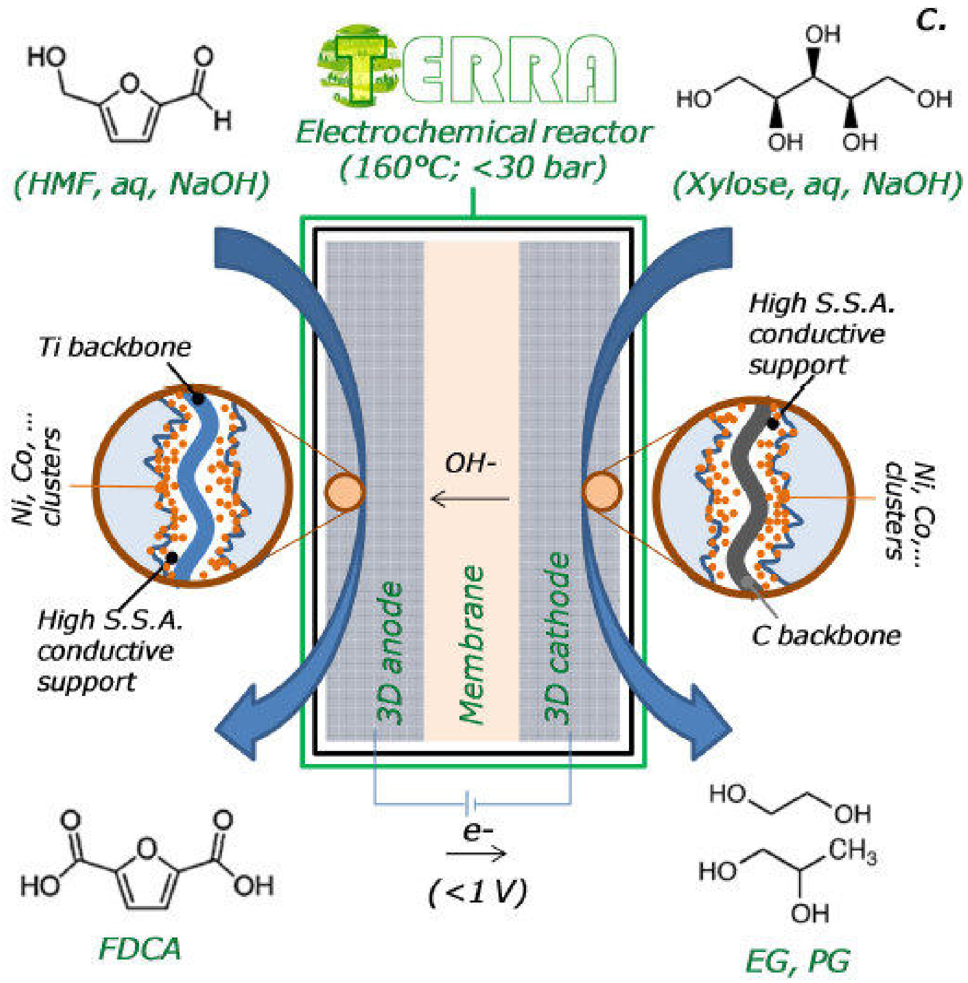
Poly(ethylene 2,5-furandicarboxylate) (PEF)

Ethylene glycol (2.2 eq.)

FDCA

TERRA Concept

Combine Ox./Red. of bio-mass derivatives (HMF + xylitol) to PEF polymer precursors (FDCA+ EG)



Catalyst Synthesis:

Metal nano-particles (MNPs)

Electrode fabrication:

MNPs on HSA 3D electrodes (TNTs/CNTs)

Testing:

at high T, P

Electrode upscaling

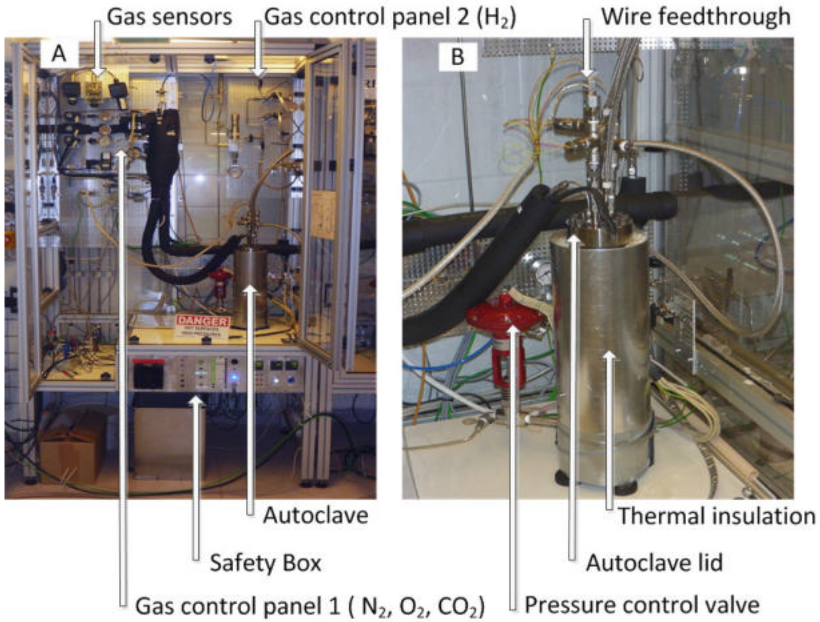
individual electrode heating

prototype development and demonstration

LCA

TERRA - Testing

Autoclave for HTP testing



T: 25 - 250 ˚C

p: 1 - 95 bar

Feed/Flow: Liquid (<10 ml/min) and/or gas (~1 L/min)

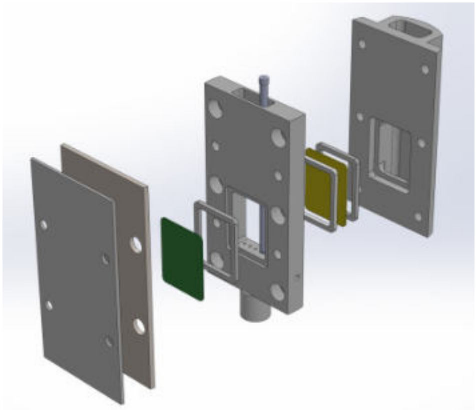
Cell size: ~5 cm^2

Atmosphere: N_2, CO_2, H_2/O_2, H_2O

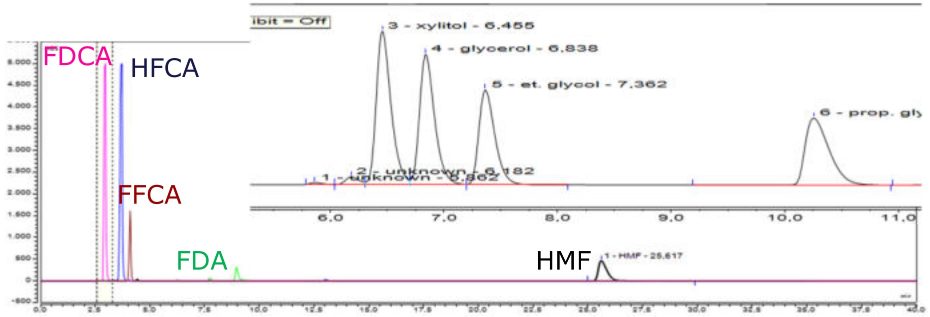
Gas/Liquid sampling for chemical analysis (GC, HPLC, etc.)

Liquid flow and sampling at HTP

Flow cell holder, mini-RE for HTP



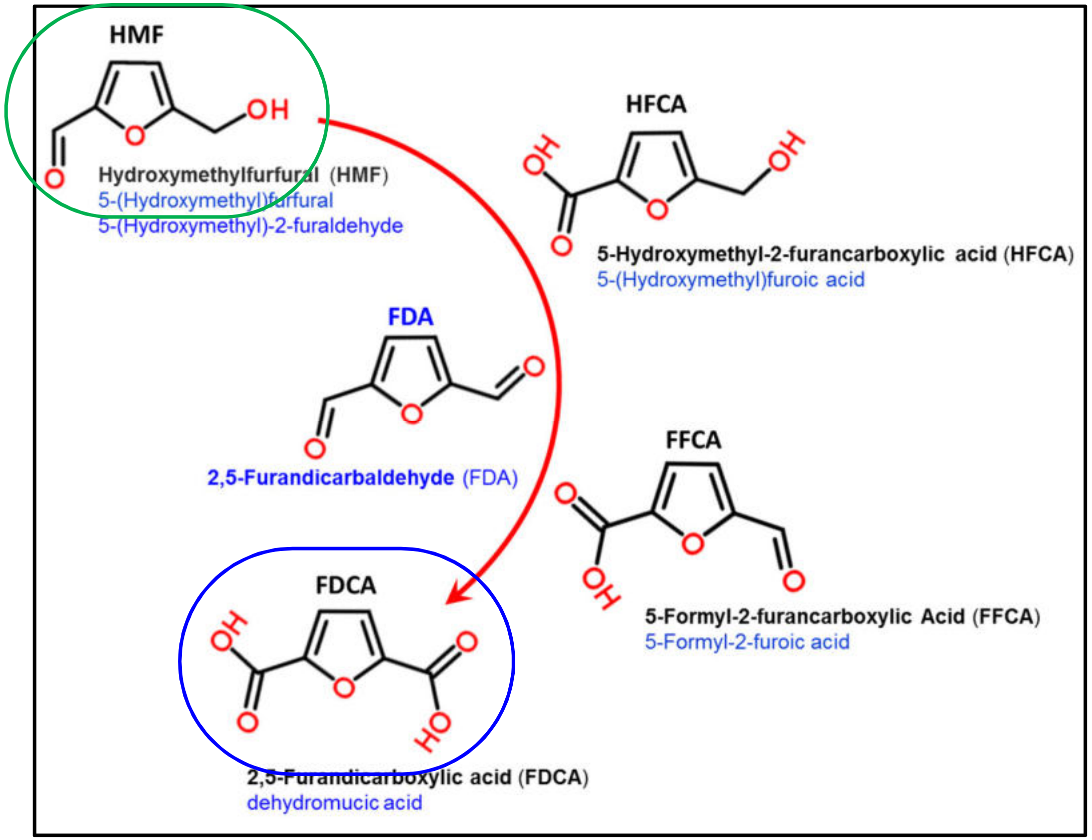
HPLC analysis for glycols (RID) and furanic acids (VWD)



❑ BIOMASS Electrolysis to Chemicals & Polymers

5-HMF Electrooxidation into 2,5-FDCA

TERRA



Hydroxymethylfurfural (HMF)
5-(Hydroxymethyl)furfural
5-(Hydroxymethyl)-2-furaldehyde

5-Hydroxymethyl-2-furancarboxylic acid (HFCA)
5-(Hydroxymethyl)furoic acid

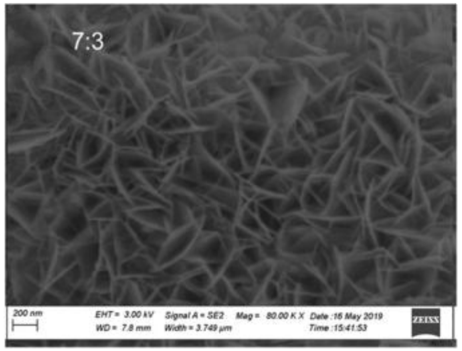
2,5-Furandicarbaldehyde (FDA)

5-Formyl-2-furancarboxylic Acid (FFCA)
5-Formyl-2-furoic acid

2,5-Furandicarboxylic acid (FDCA)
dehydromucic acid

TERRA – HMF electro-oxidation

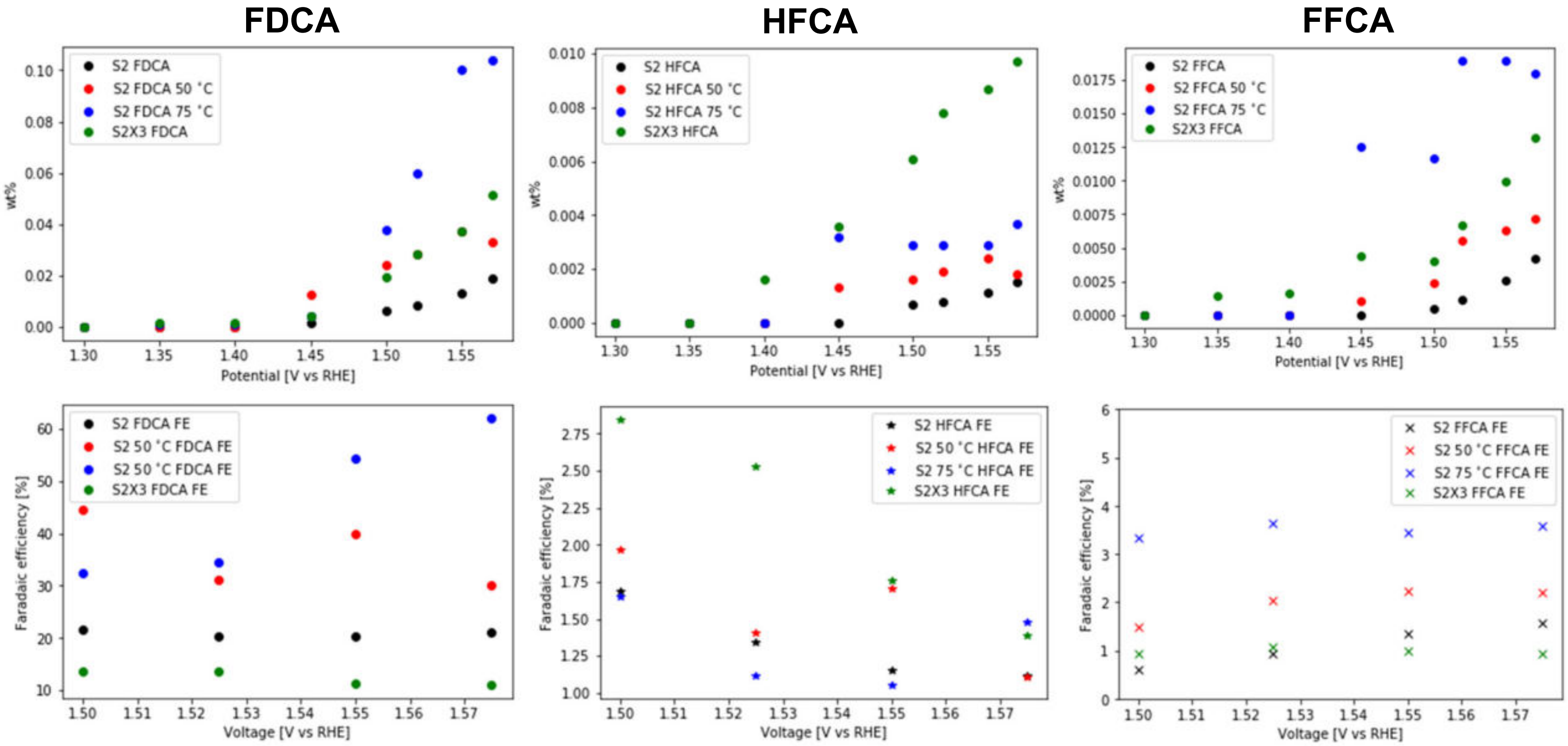
$Ni_{0.7}Fe_{0.3}OOH$@Ni-Foam



S2 = 10 mM HMF + 100 mM KOH

(Flow rate = 1 mL/min)

Separate HMF and KOH streams



- FDCA selectivity of 75% at 1.575 V vs. RHE at 75°C (corresponding FDCA FE of 60%) @50% HMF Conversion

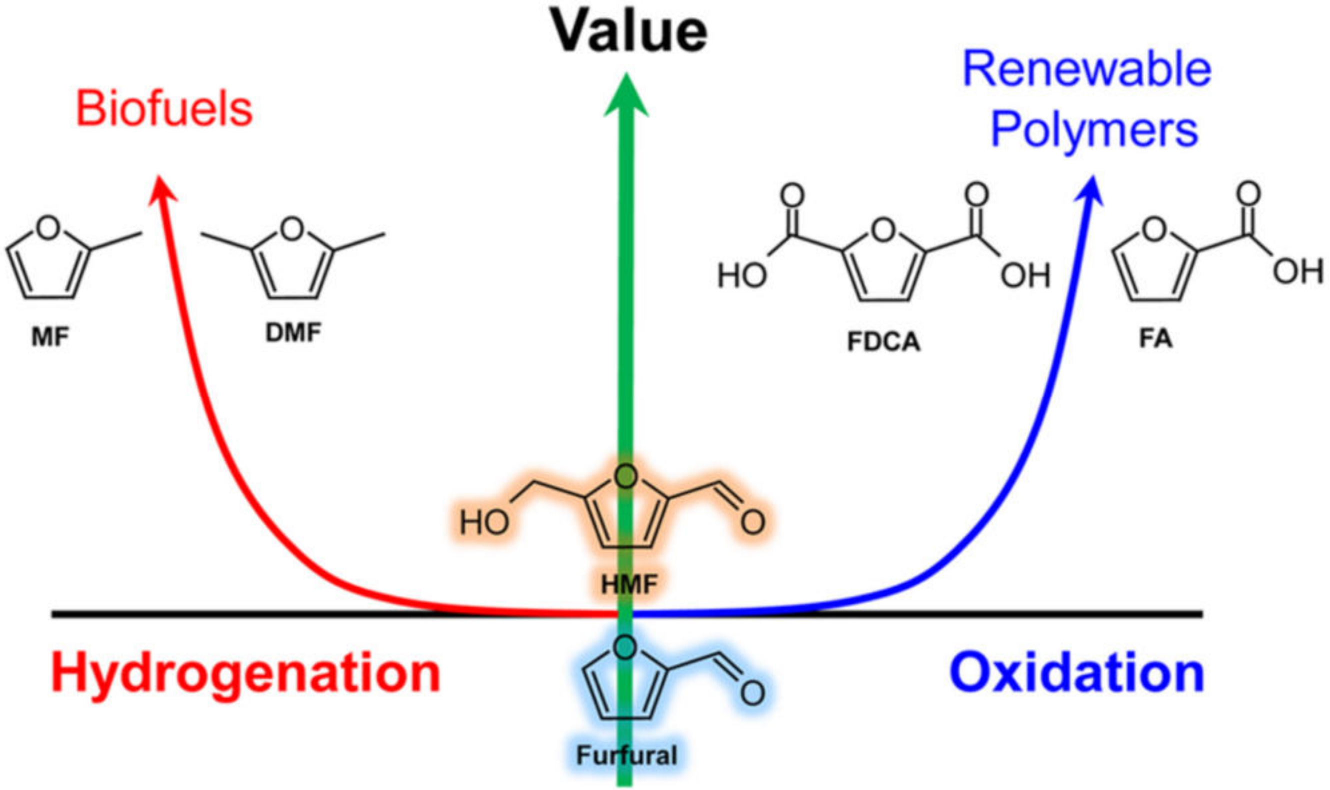
Other activities on HMF

Electrocatalytic Conversion of Furanic Compounds

Youngkook Kwon,[†,‡] Klaas Jan P. Schouten,[†,§] Jan C. van der Waal,[§] Ed de Jong,[§] and Marc T. M. Koper[*,†]

[†]Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands
[‡]Carbon Resources Institute, Korea Research Institute of Chemical Technology, Daejeon 34114, Republic of Korea
[§]Avantium Chemicals, Zekeringstraat 29, 1014 BV Amsterdam, The Netherlands

DOI: 10.1021/acscatal.6b01861
ACS Catal. 2016, 6, 6704–6717

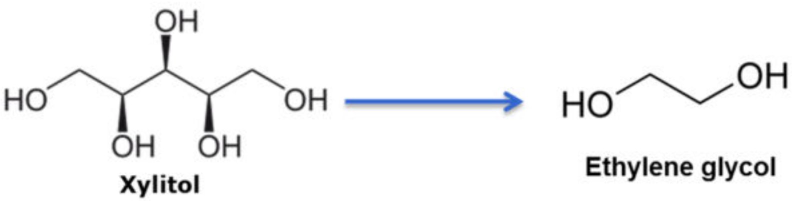


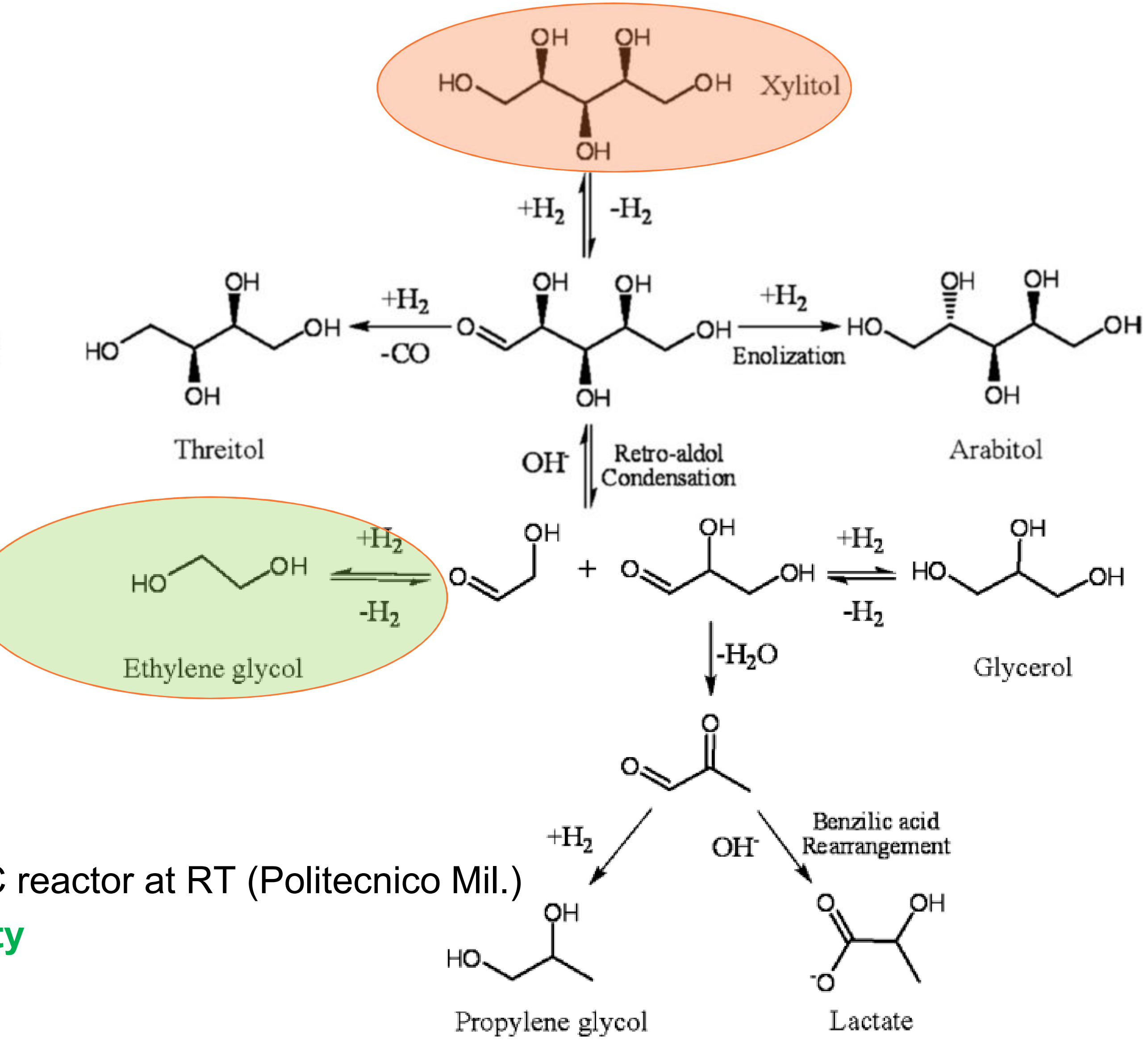
EC FDCA synthesis

other groups:

Schumann, Bochum
Strasser, Berlin
….

Xylitol reduction

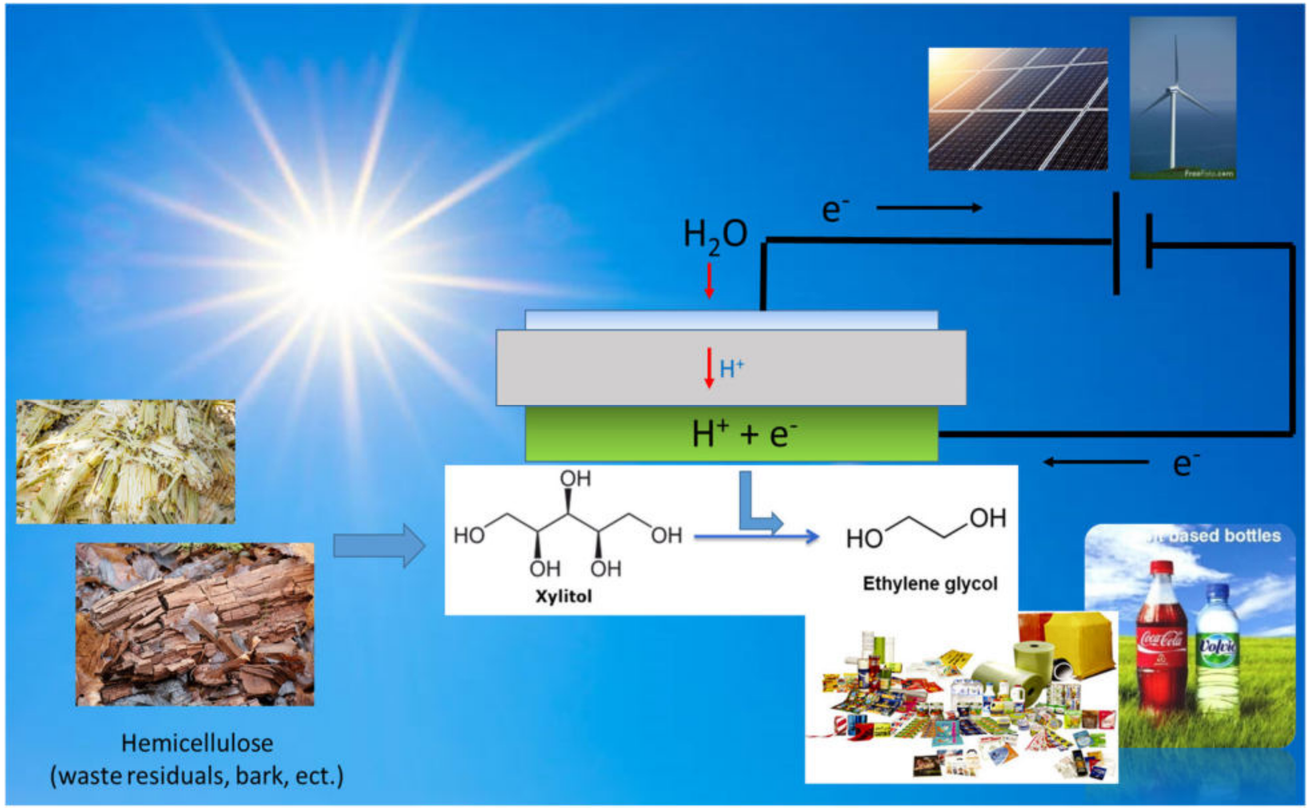




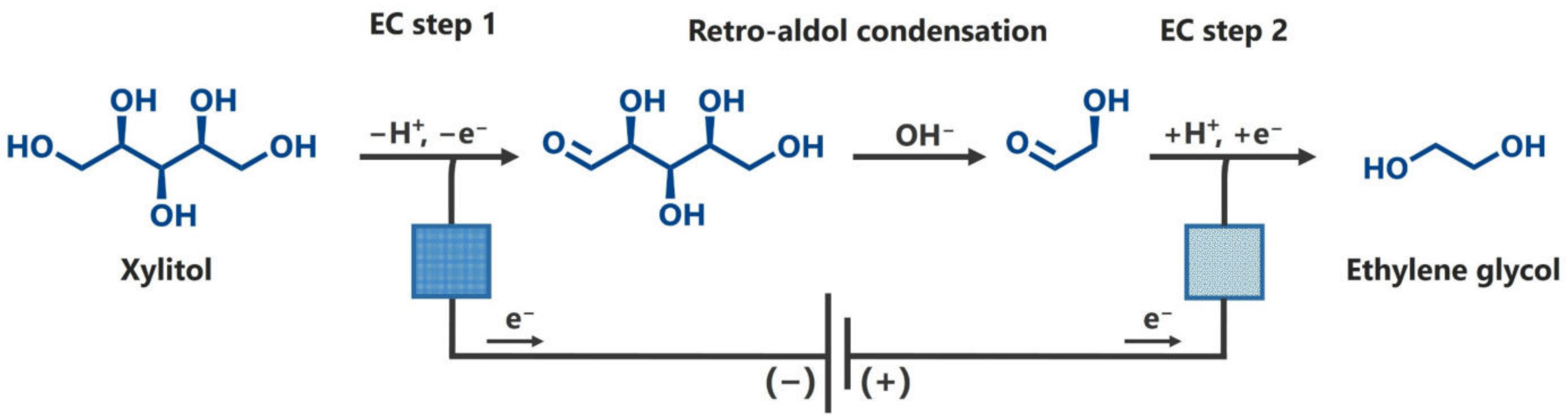
- Multiple steps
  - Dehydrogenation
  - Hydrogenation
  - Various possible products

- Principle proven in batch EC reactor at RT (Politecnico Mil.)
  - **Relatively high selectivity**
  - **Low conversion rate**

Project idea “OrganicES”, IRFD, DK, start Jan 2022



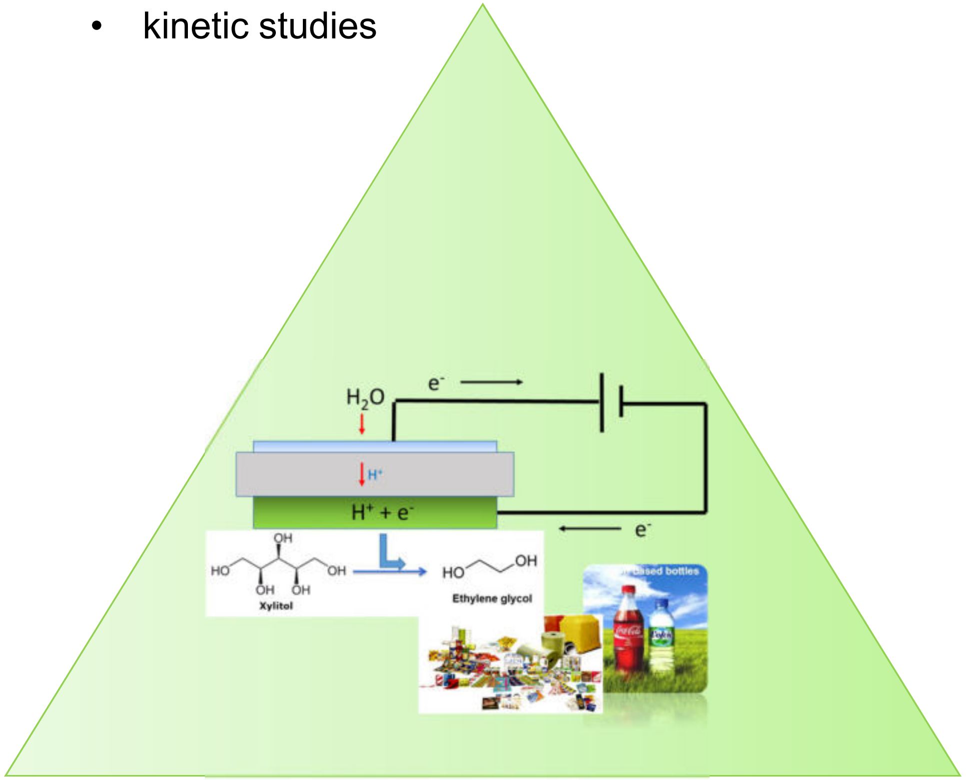
Paired reactions in a flow reactor?



Scientific aspects and research objectives

process integration in flow reactors

- kinetic studies



Electrocatalysts design

- DFT Modelling
- Synthesis and charaterization

Reaction mechanisms

- DFT modelling
- Experimental validtaion

Acknowledgement

Thank You for Your attention

David Tran

Christos Chatzichristodoulou

Khurram S.Joya

Marie Lund Traulsen

Florian Gellrich

Mathias Christensen

EU Grant Agreement 677471

OrganicES

INDEPENDENT RESEARCH
FUND DENMARK

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

Development of thin electrode layers by spray coating for solid oxide cells

M. Jacobs[a], L.O. Jøsang[b] and V. Middelkoop[a]

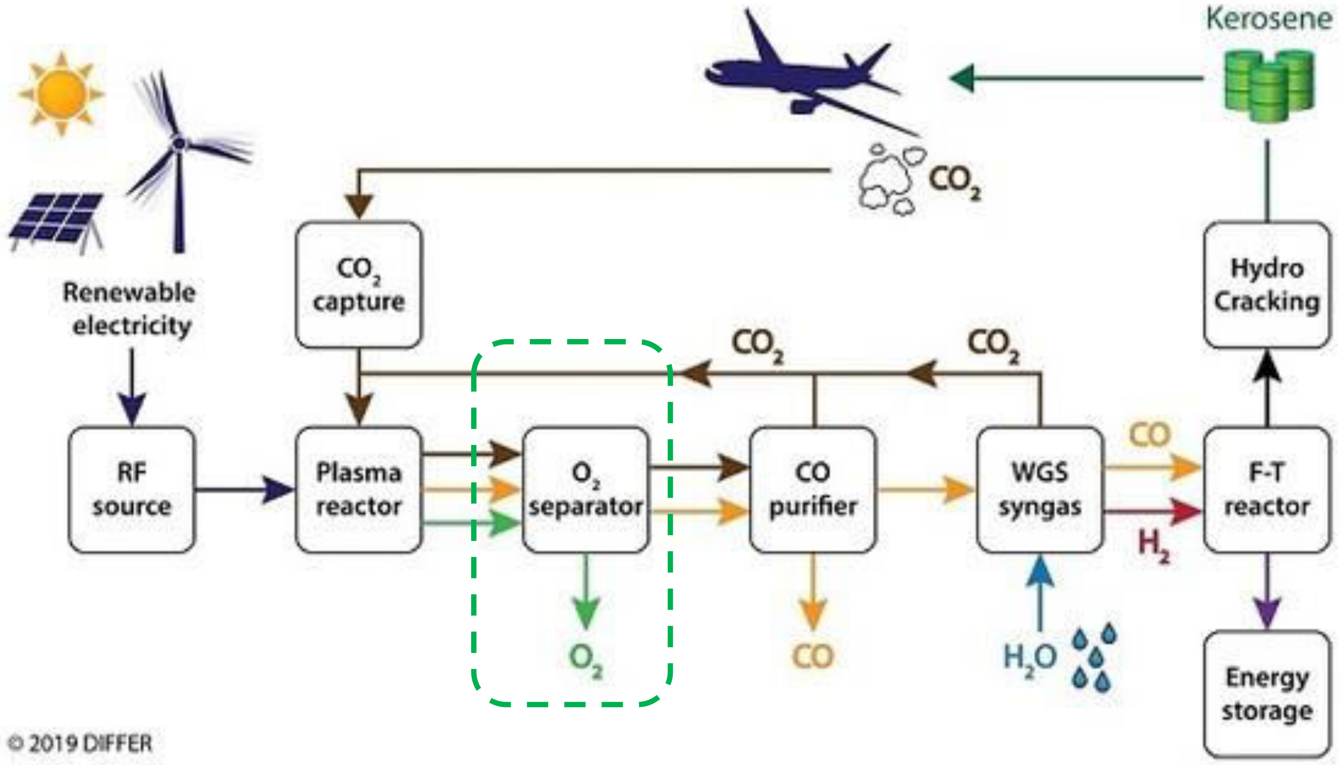
[a] Flemish Institute for Technological Research – VITO, Boeretang 200, B-2400 Mol, Belgium
[b] Ceramic Powder Technology AS – CerPoTech, Kvenildmyra 6, N-7072 Heimdal, Norway

Winter school, February 10th 2022, online

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

H2020 KEROGREEN project

- Partners: DIFFER (NL), CerPoTech (NO), HyGear (NL), KIT (DE), INERATEC (DE) and VITO (BE)
- Focus on O_2 separator
  - Based on solid oxide cell
  - Perovskite based electrodes



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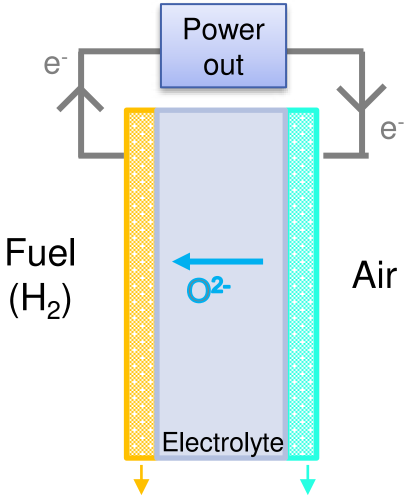
SOEC vs SOFS vs oxygen separator

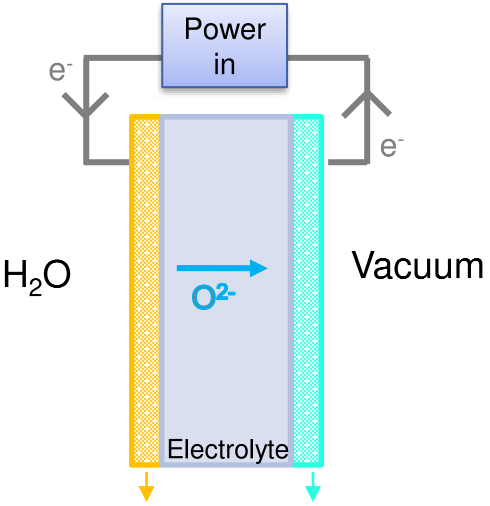
SOFC



Fuel electrode
$H_2 + O^{2-} \rightarrow H_2O + 2e^-$

Oxgen electrode
$1/2O_2 + 2e^- \rightarrow O^{2-}$

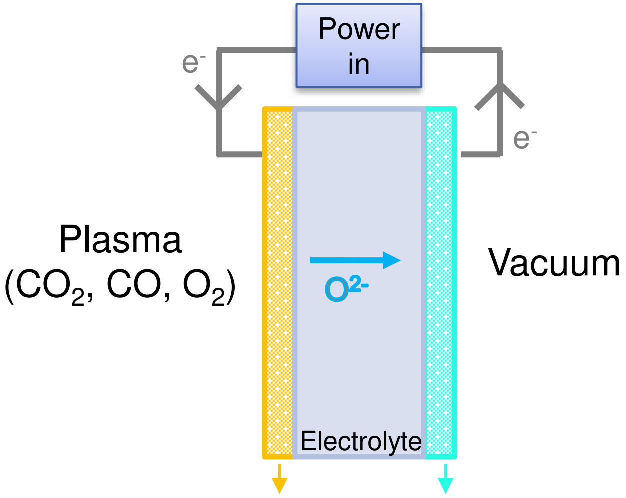
SOEC



Fuel electrode
$H_2O + 2e^- \rightarrow O^{2-} + H_2$

Oxgen electrode
$O^{2-} \rightarrow 1/2O_2 + 2e^-$

Oxygen separator



Plasma electrode
$O_2 + 2e^- \rightarrow 1/2O^{2-}$

Oxgen electrode
$O^{2-} \rightarrow 1/2O_2 + 2e^-$

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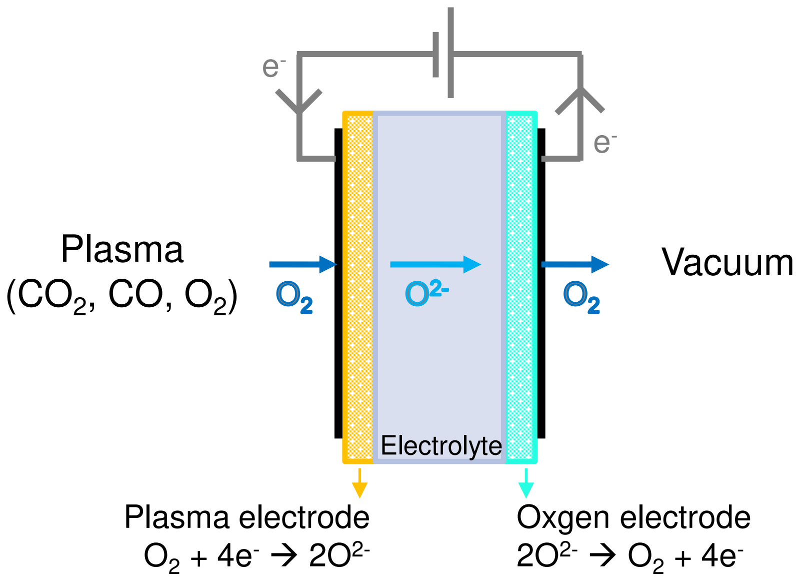
Oxygen separator

- General
  - High oxygen fluxes
  - Stability
- Both electrodes
  - Mixed ionic and electronic conductivity
- Electrolyte
  - Oxygen ion conductivity
  - Low resistance
- Plasma electrode
  - Poor activity for CO oxidation

Selected materials
- Electrolyte: 8-YSZ
- Oxygen electrode: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)
- Plasma electrode: $La_{0.4}Sr_{0.4}Zn_{0.12}Ti_{0.88}O_3$ (LSZT)
- Interlayer: $Ce_{0.8}Gd_{0.2}O_2$ (GDC)

Oxygen separator



Plasma electrode
1) Electrochemical O_2 separation: $O_2 + 4e^- \rightarrow 2O^{2-}$
2) CO_2 electrolysis: $CO_2 + 2e^- \rightarrow CO + O^{2-}$
3) CO oxidation: $2CO + O_2 \rightarrow 2CO_2$

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Manufacturing/characterisation of powders

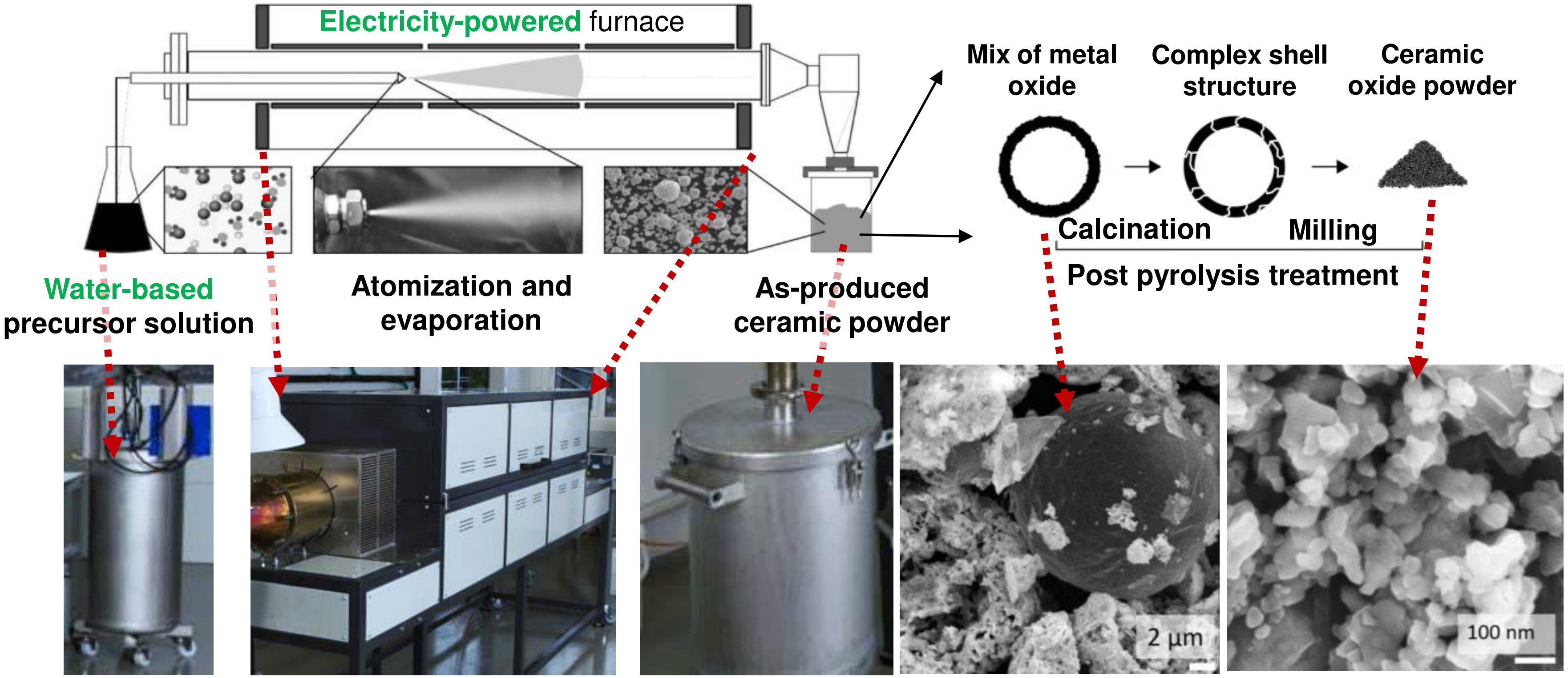
Powder manufacture by spray pyrolysis

Major manufacture steps:

1) Prepare water-based solution, containing required cations

2) Spray the solution into hot furnace

3) As-sprayed powder is post-processed, i.e.
- Calcined;
- Milled;
- Dried;
- Sieved;
- Analyzed by XRD, BET, SEM



Tank with metal salts solution

Pyrolysis furnace

Powder collector

Agglomerates: 1-50 µm

Particles: 10-500 nm
SSA in range 1-50 m^2/g

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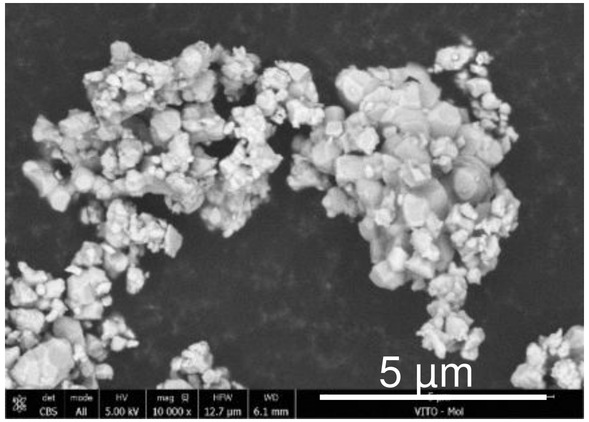
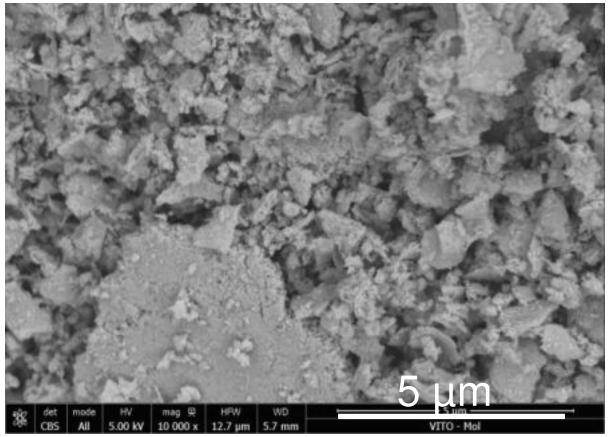
Manufacturing/characterisation of powders

LSCF



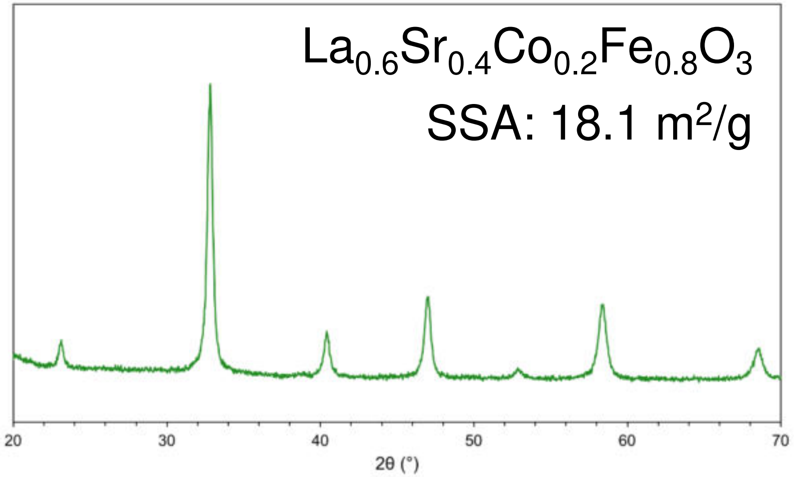
d50 of 13 µm

LSZT



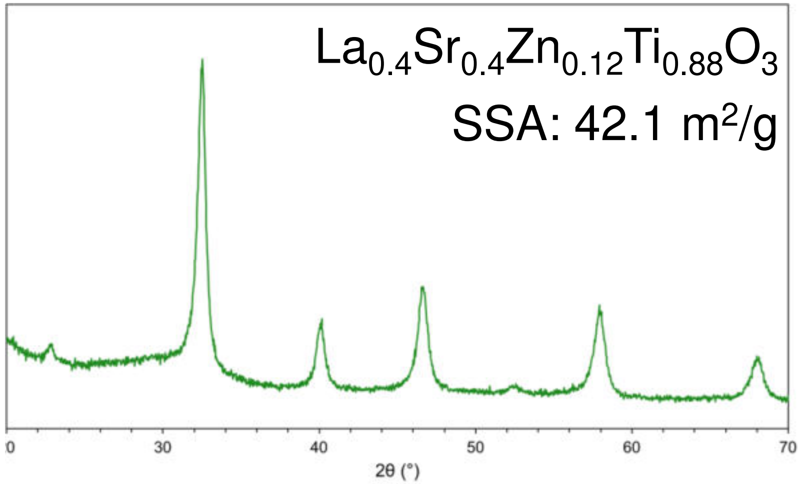
d50 of 250 µm

- Particle size of LSCF much finer than LSZT
- XRD patterns of all the materials exhibit single phase pattern



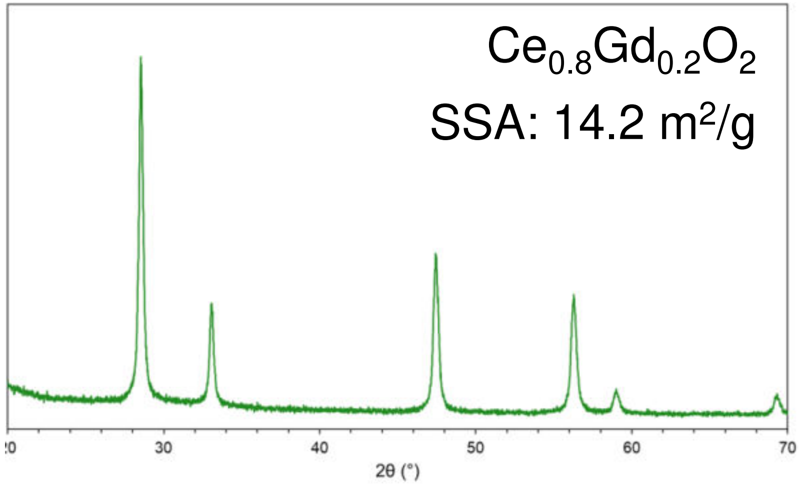
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$

SSA: 18.1 m²/g



$La_{0.4}Sr_{0.4}Zn_{0.12}Ti_{0.88}O_3$

SSA: 42.1 m²/g



$Ce_{0.8}Gd_{0.2}O_2$

SSA: 14.2 m²/g

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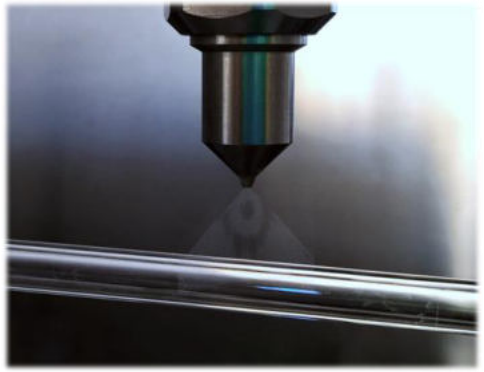
Why spray coating?

	Suspension viscosity	Scalable	Substrate geometry	Thickness control
Spray coating	Low	Yes	Non-flat	High
Dip coating	Wide range	Yes	Non-flat	Medium
Spin coating	Wide range	No	Flat	Medium
Screen printing	High viscosity	Yes	Flat	High
Slot-die coating	Wide range	Yes	Flat	High
Tape casting	High viscosity	Yes	Flat	Low
CVD	/	No	Flat	High



Spray coating

- Greater **control** of the **thickness**
- Accommodation of **large substrates**
- Ability of **porous layers** on planar and tubular substrates

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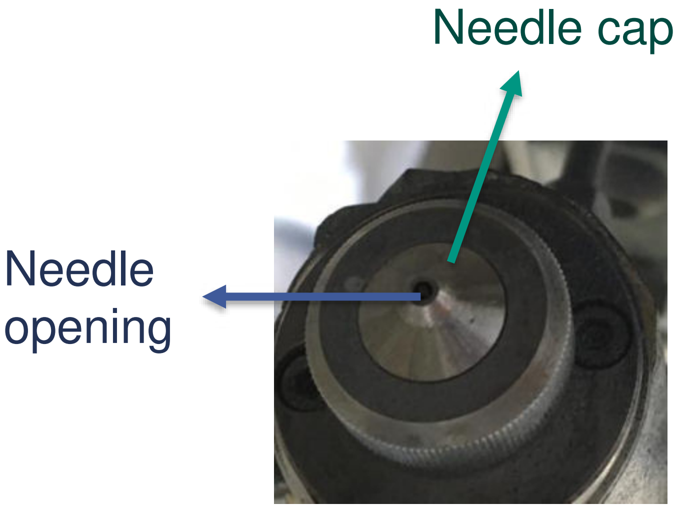
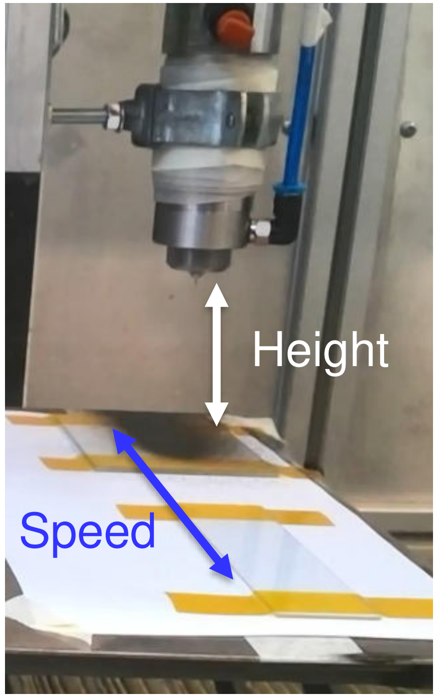
Spray coating: principle

- Variable parameters:
  - Atomisation pressure
  - Flow rate of suspension
  - Linear speed of spray gun
  - Height of spray gun (distance between spray nozzle and substrate)
  - Needle opening
  - Needle cap





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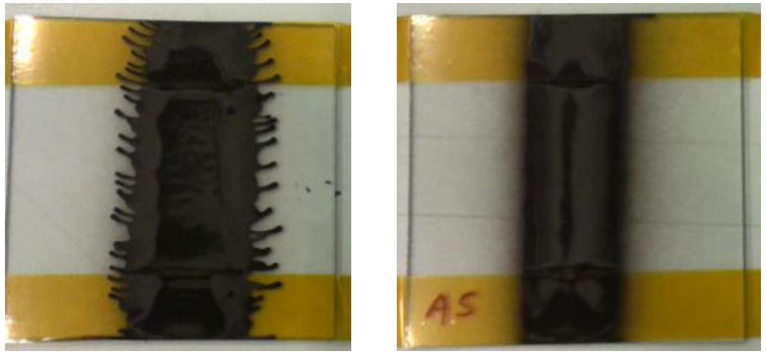
Spray coating: optimization of parameters

Effect of linear speed

2 m/min | 1 m/min | 0,5 m/min

Effect of height



4 cm | 6 cm

Effect of atomization pressure

0,5 bar | 1 bar | 2 bar

Effect of flow rate

1,5 ml/min | 3 ml/min

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Suspension - composition

- Composition of suspension based on literature and previous knowhow
  - Solvent: ethanol
    - Allows fast drying of coating layer so that multiple coating layers can be applied shortly after each other
  - Additives: Ethyl cellulose, Polyvinylpyrrolidon, Polyvinyl butyral
    - To have optimal viscosity for spraying
    - To avoid agglomeration of suspension
    - To have good adhesion on substrate
    - To obtain homogeneous coatings

	EC (m%)	PVP (m%)	PVB (m%)
KER-LSCF-000	19,0	1,2	0
KER-LSCF-001	19,0	0	1,2
KER-LSCF-002	18,2	0	5,7
KER-LSCF-003	0	1,2	19,0
KER-LSCF-004	0	5,7	18,2
KER-LSCF-005	8,7	0	26,2
KER-LSCF-006	18,8	1,2	1,2

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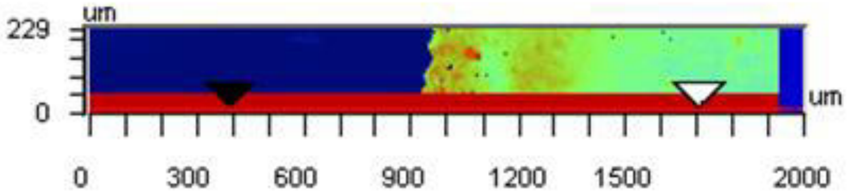
Suspension - composition

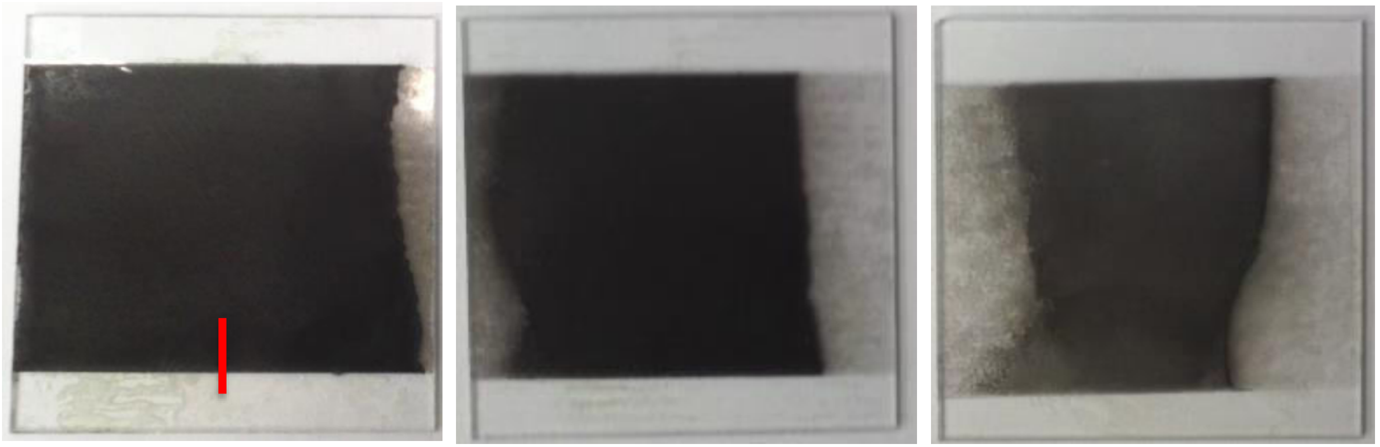
- Each suspension was spray coated with different speeds on glass substrate, just one layer
- At one speed, 3 coating layers were applied
- Thickness of coating was determined by optical profilometry



1,5 m/min

3,0 m/min

6,0 m/min



Line scan profilometry

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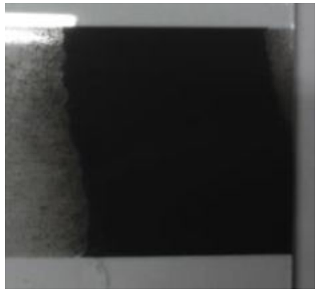
Suspension - composition

→ Addition of extra binder PVB seems to improve coating, visually and its thickness

Coating speed [m/min] → Thickness [µm]	1,5	3,0	6,0	3x 3,0
LSCF 001	1,6	4,1	1,4	14,4
LSCF 002	9,2	5,1	5,1	17,7
LSCF 003	2,6	3,2	2,3	26,6
LSCF 004	<1	16,2	4,2	5,5
LSCF 005	11,0	6,8	5,3	15,1
LSCF 006	9,9	6,0	4,5	21,0


001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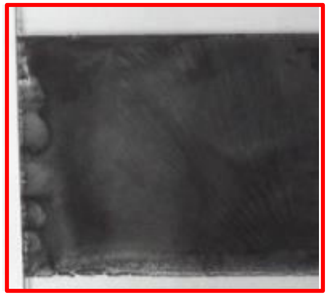
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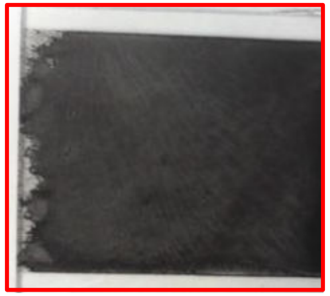
004


005


006

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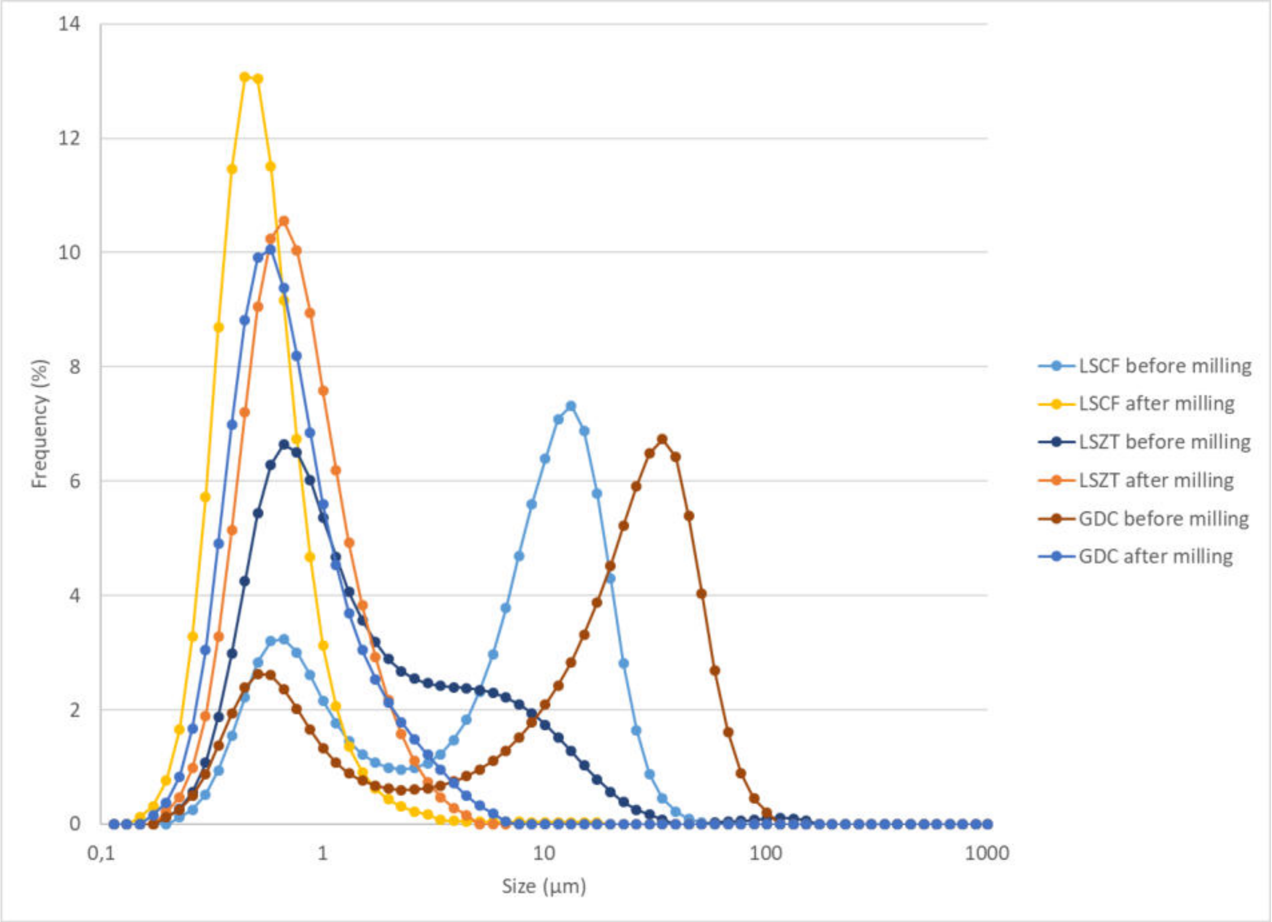
Suspension - milling

Why milling?

- To spray without blockages
- To improve homogeneity
- To have dense interlayer after thermal treatment

0 min	LSCF	GDC	LSZT
d10 /µm	0.54	0.51	0.43
d50 /µm	7.59	17.69	1.08
d90 /µm	17.63	44.81	7.89

5 min	LSCF	GDC	LSZT
d10 /µm	0.28	0.33	0.37
d50 /µm	0.47	0.61	0.68
d90 /µm	0.87	1.67	1.48



→ Large reduction of particle size, even after 5 min of milling

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Suspension - milling

Why milling?

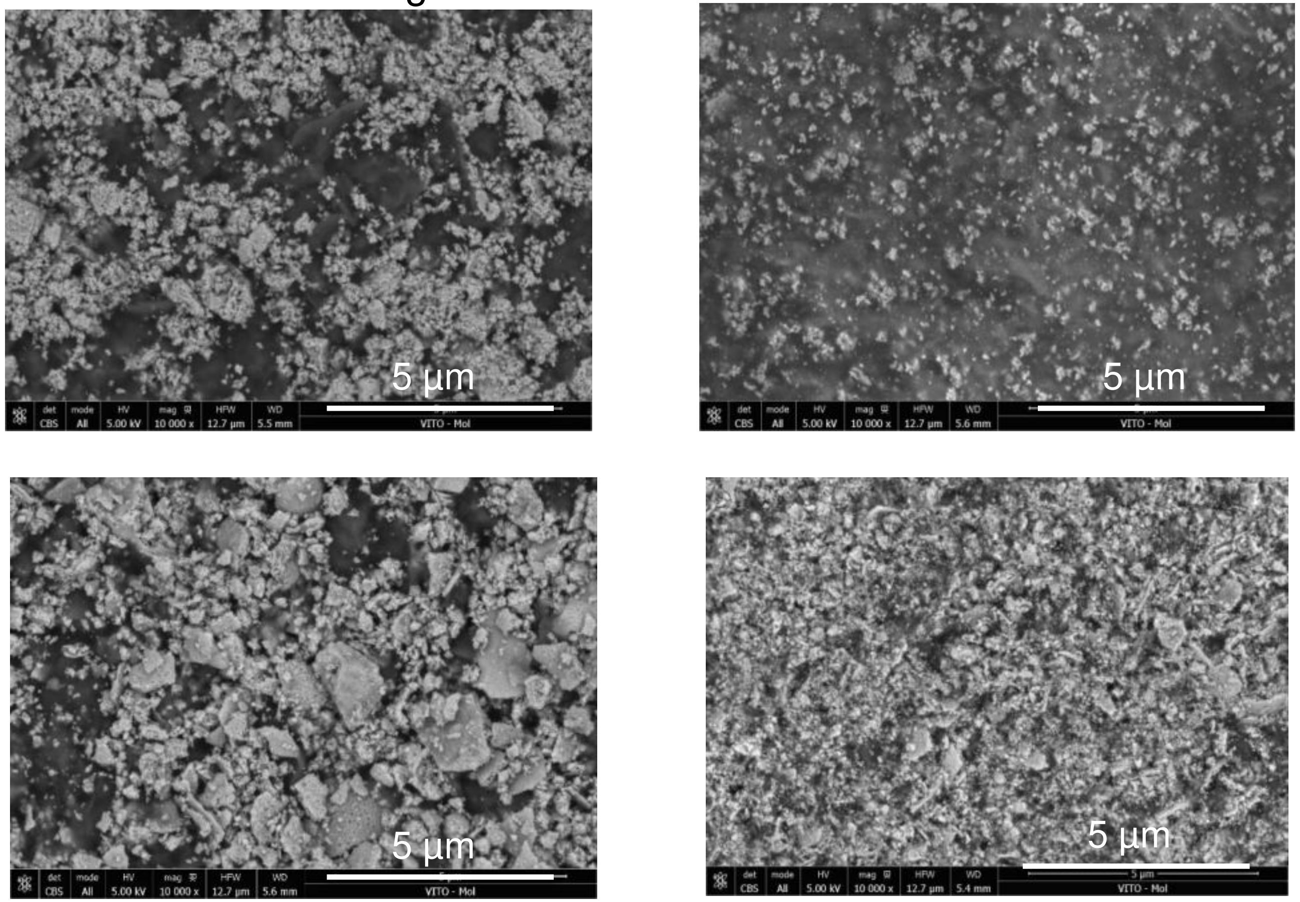
- To spray without blockages
- To improve homogeneity
- To have dense interlayer after thermal treatment

Before milling

After milling

LSCF

LSZT



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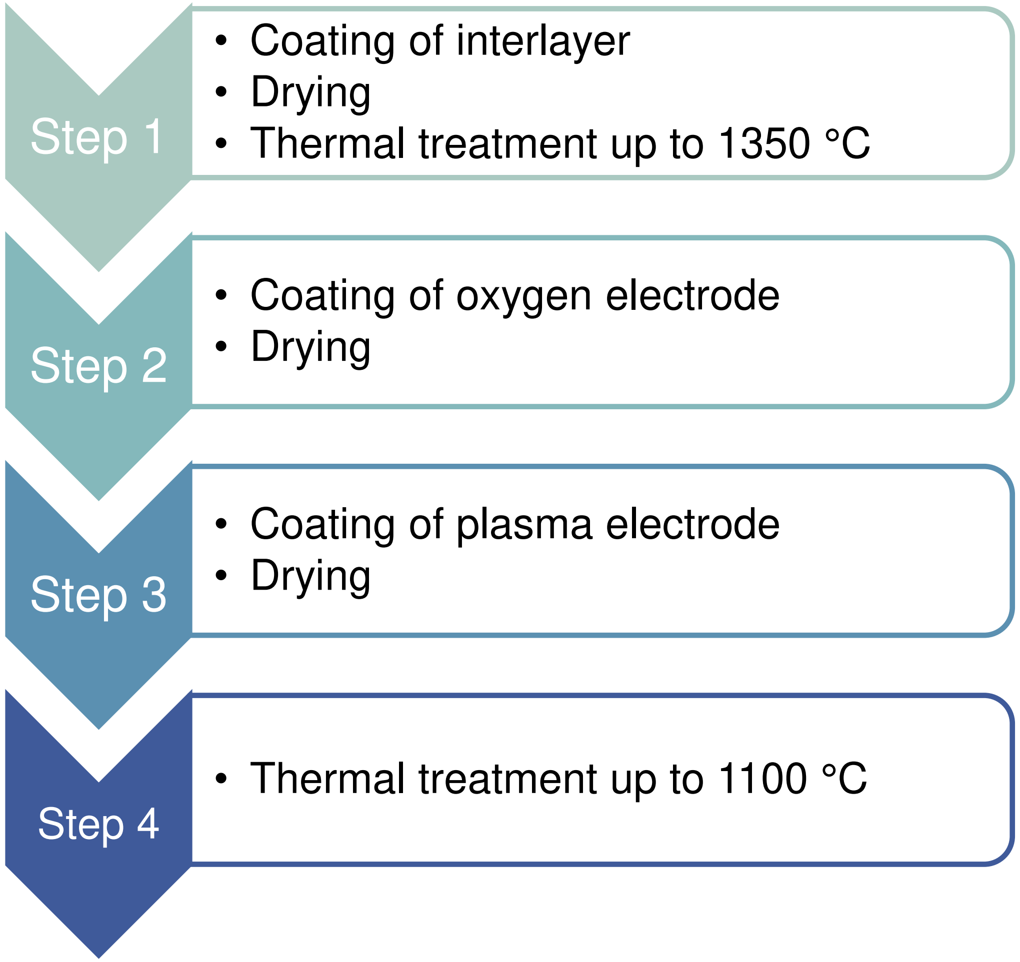
Spray coating of SOC



Step 1

- Coating of interlayer
- Drying
- Thermal treatment up to 1350 °C

Step 2

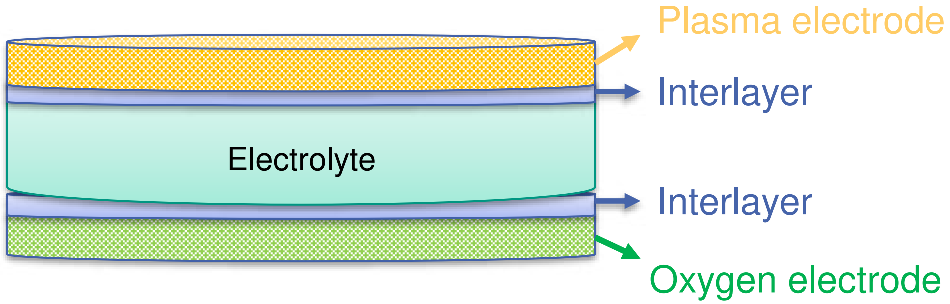
- Coating of oxygen electrode
- Drying

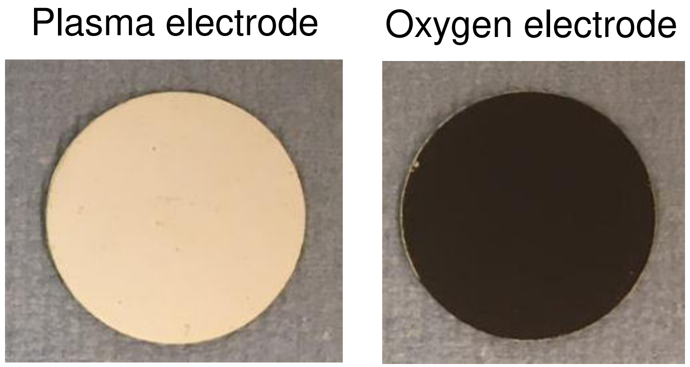
Step 3

- Coating of plasma electrode
- Drying

Step 4

- Thermal treatment up to 1100 °C





20 mm Ø
200 µm thickness

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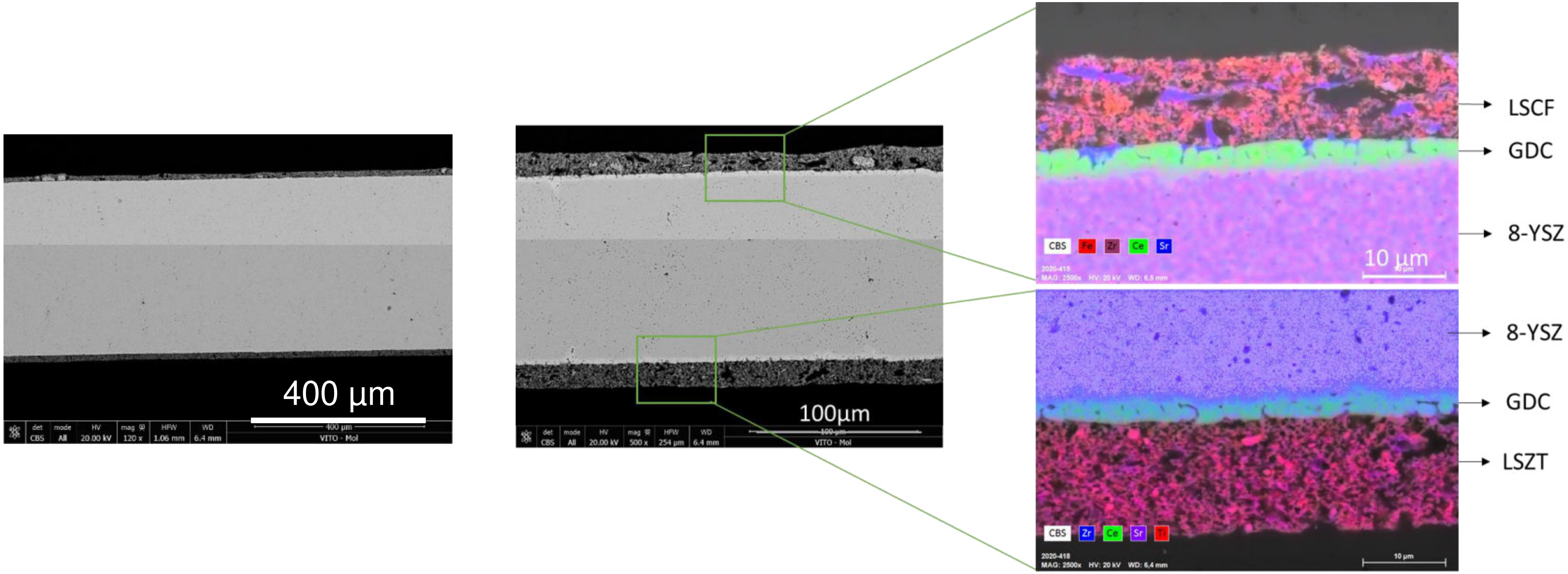
Microstructural characterisation of SOEC



SEM images of cross-section of YSZ discs coated with GDC thin dense interlayer, LSCF (10-15 µm) oxygen electrode and LSZT (20 µm) as plasma electrode

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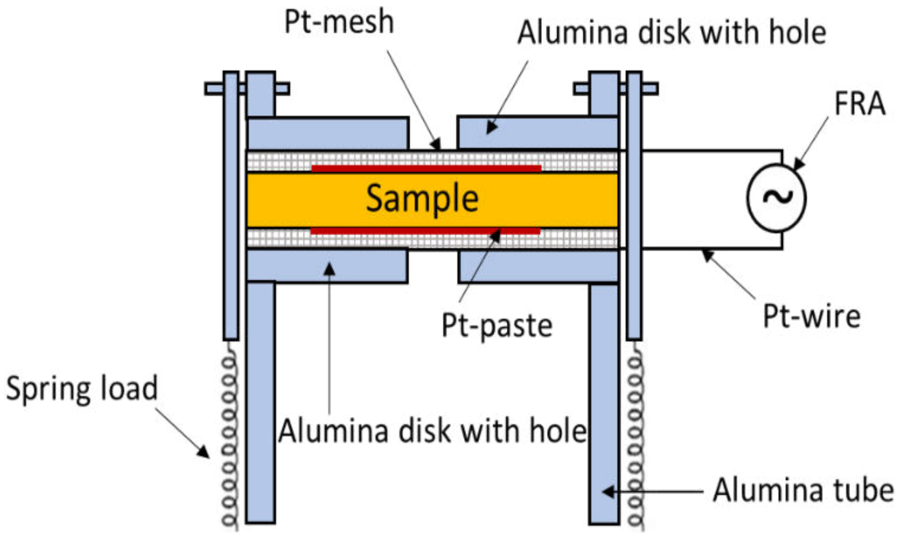
EIS – set-up/conditions

- EIS: technique to measure the impedance of a system in dependence of the AC potentials frequency
    - Used to analyse the performance of SOFC/SOEC/batteries
    - Often plotted by a Nyquist plot

- Testing conditions:
    - Atmosphere: Dry Air (flow rate: 50 cc/min)
    - Temp: 800ºC-500ºC (ramp rate: 3 ºC/min)
    - Steady state: 24 hours
    - EIS characterization: 2 MHz to 0.01 Hz



Winter school, February 10th 2022, online

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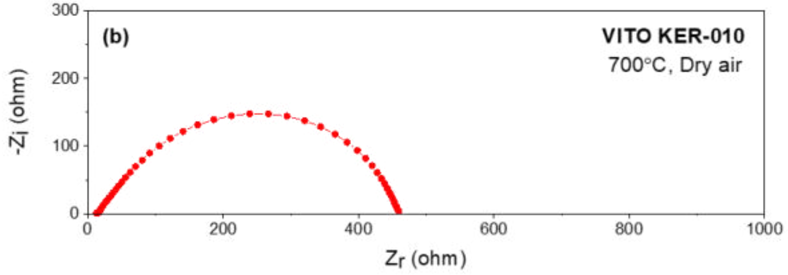
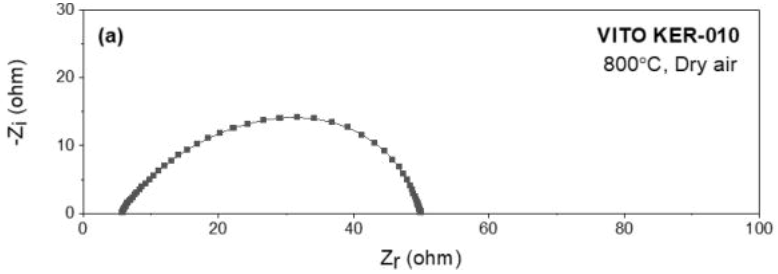
EIS - results

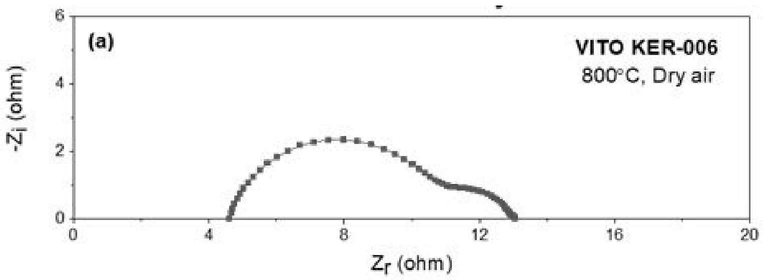
700 °C
Without interlayer



800 °C
Without interlayer



800 °C
With interlayer



Reduced resistance

- By increasing temperature
- By adding GDC interlayer

LSCF

LSZT

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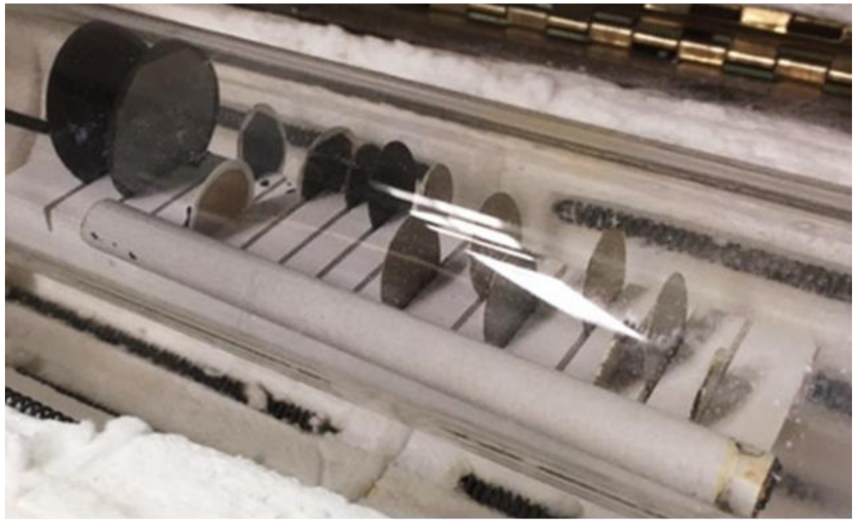
Stability test under CO_2/CO/O_2 atmosphere (=plasma atmosphere)

- Why: Test was done to simulate long time exposure to plasma environment and to study stability of plasma electrode
- How: 2 weeks exposure to CO_2/CO/O_2 gas atmosphere at 800 °C
  - XRD of surfaces
  - SEM/EDS of surfaces and cross-section



Different solid oxide cells in the reactor for the stability test

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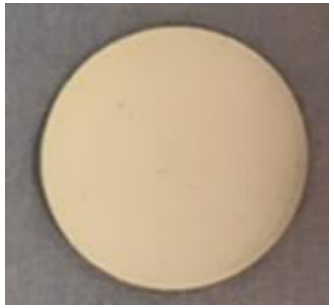
Stability test under $CO_2/CO/O_2$ atmosphere (=plasma atmosphere)

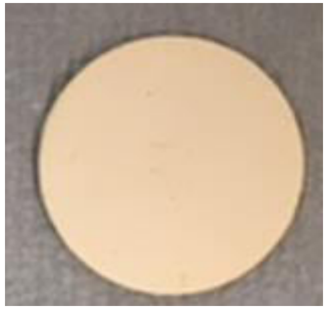
LSZT based electrolyte supported cell:

- Visual: No changes visible
- SEM/EDS: No interactions between the layers observed on EDS mappings
- XRD: No phase changes can be observed after thermal and chemical stability test

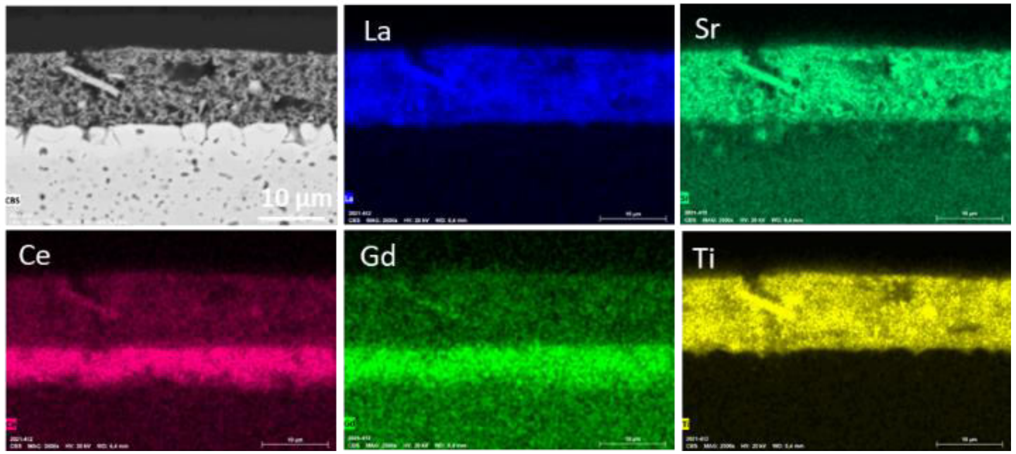
Before

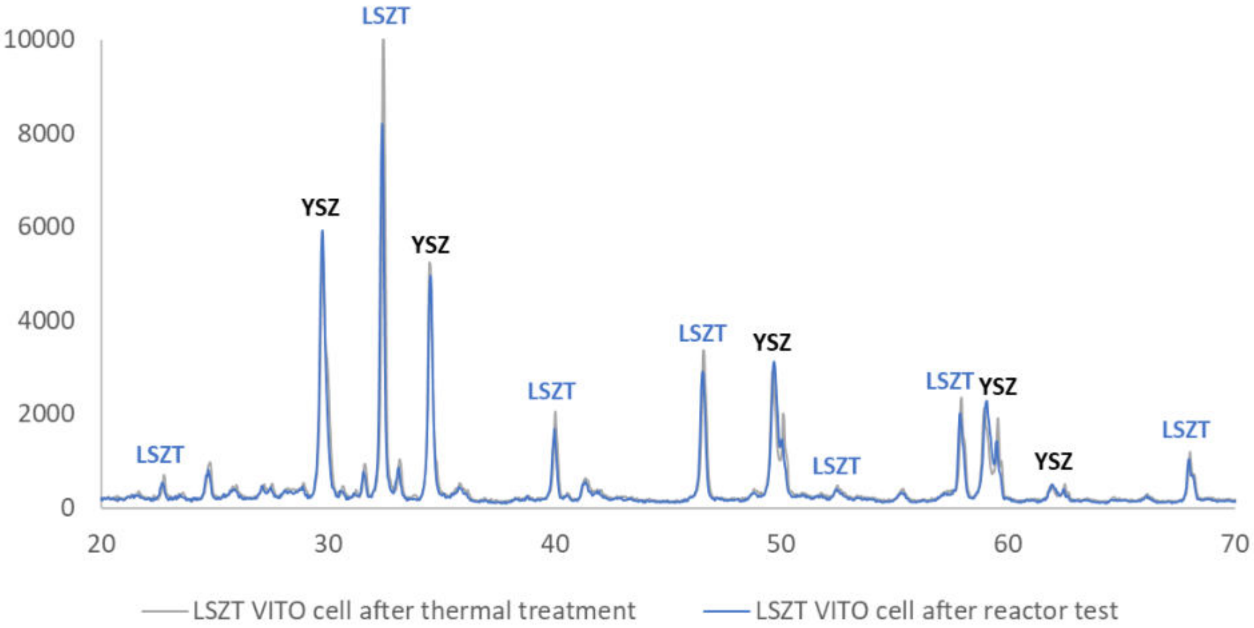


After



After thermal & chemical stability test





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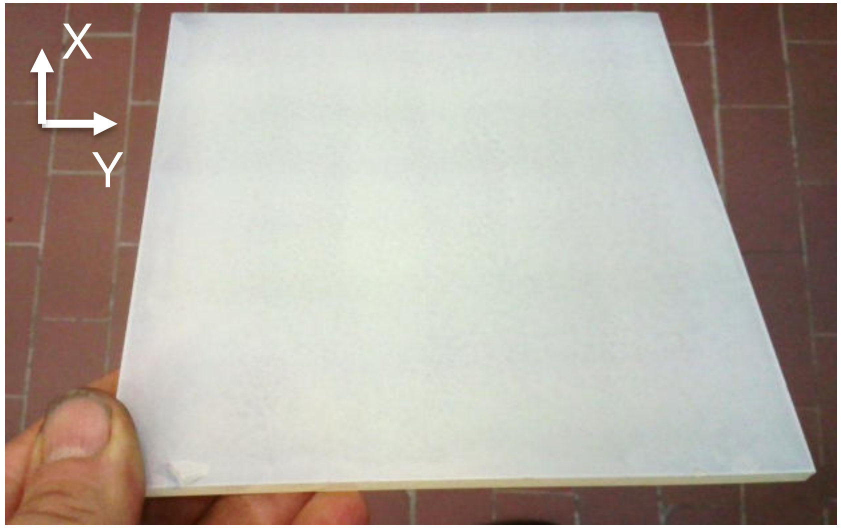
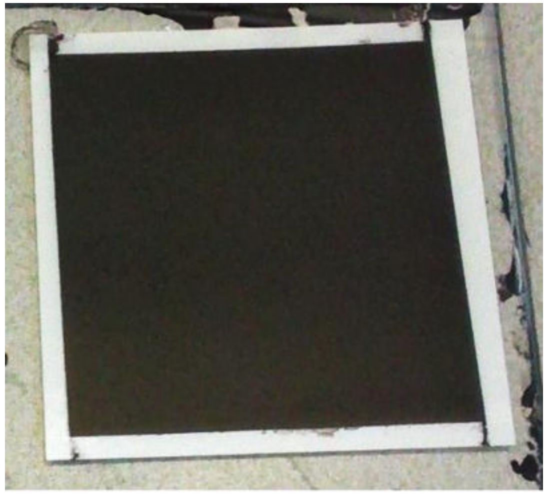
Upscaling

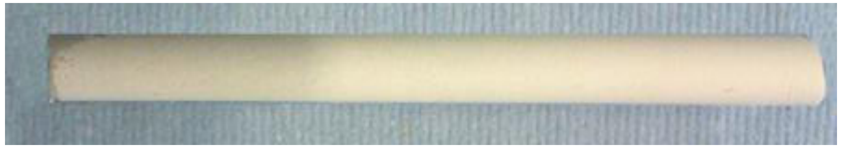
- Upscaling of spray deposition of larger SOEC substrates
  - Step in Y-direction is important to have homogeneous coating (X: coating direction)
- Development of tubular SOECs
- Development of electrode based SOECs



GDC coating on 200x200 mm^2 glass substrate



Oxygen electrode on 50 x 50 mm^2 cells



Tubular SOEC

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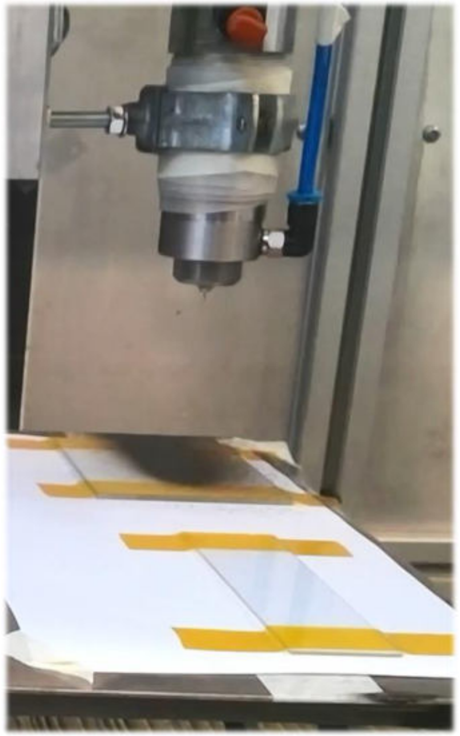
Conclusions

- Oxygen separator based on SOEC was selected for the removal of oxygen from the plasma atmosphere
- Single phase electrode powders were successfully manufactured by spray pyrolysis
- Spray coating was used for the deposition of the electrode layers of the SOEC
- Uniform, thin porous electrode layers and dense interlayer were obtained by:
  - Optimization of the coating parameters (atomization pressure, coating speed,…)
  - Optimization of the suspension properties (formulation, particle size, viscosity)
- Upscaling of spray coating process is possible to obtain larger SOEC and tubular SOEC
- SOECs with interlayers exhibited a lower resistance than those without interlayers



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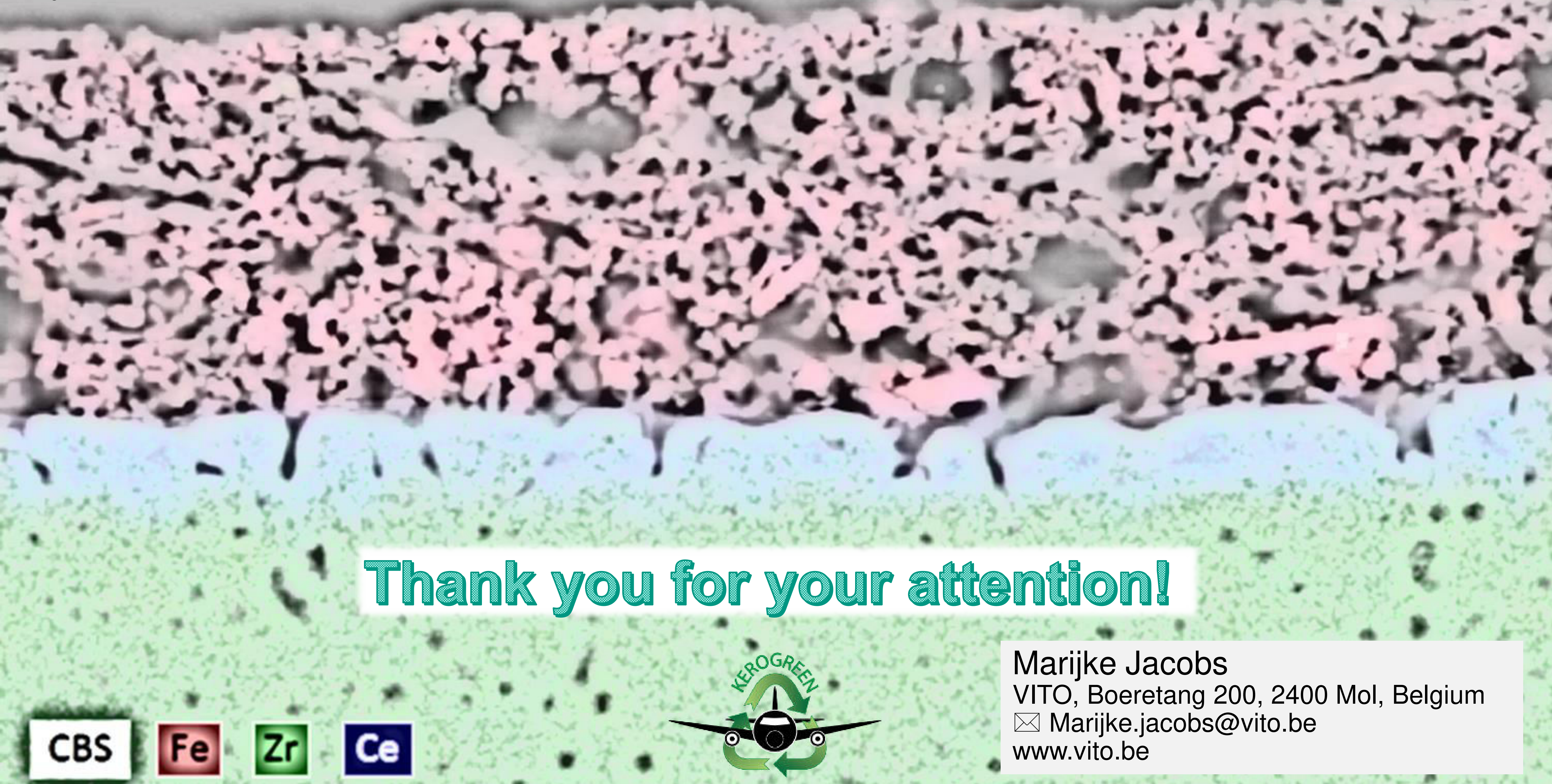

Thank you for your attention!

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Programme under GA-Nr. 763909

VTT

Vafa Järnefelt

Research Scientist

The potential of CCU technologies in mitigating climate change

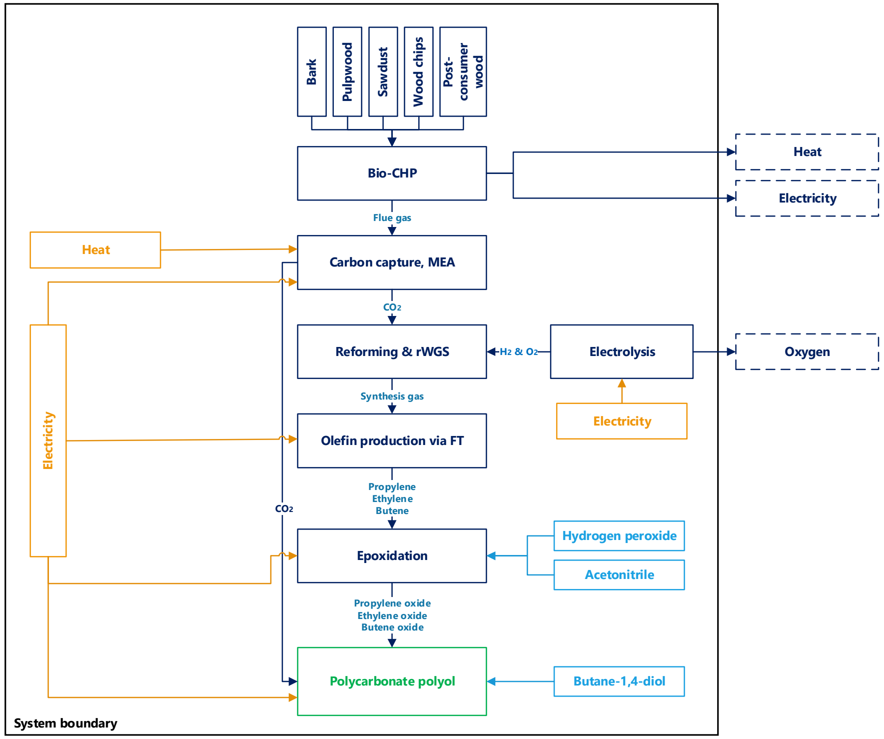
Winter School

#VTTBeyondtheObvious
@vafajarnefelt

BECCU project's CCU concept for the production of polyols

BECCU project's CCU concept for the production of polyols

- Developing the recovery of biogenic carbon dioxide and its use in the manufacture of specialty chemicals for the production of (polycarbonate) polyols.
- Polycarbonate polyols are used in the manufacture of various polyurethanes such as
  - Adhesives
  - building insulation boards
  - and goods (e.g., as shoes and mattresses).



Environmental sustainability of the BECCU concept

- Objective: to quantify the carbon footprint and other relevant environmental impact categories (e.g., fossils resource depletion, acidification, eutrophication, toxicity) to evaluate the environmental sustainability of various alternatives of BECCU solution in comparison to conventional ways to produce polyols.

The challenges of the environmental sustainability assessments of the CCU technologies

Life cycle approach

Quantification of potential environmental impacts and benefits covering the whole life cyle

Why life cycle assessment (LCA)?

Enables the minimization of the overall environmental impacts

- Systematically made overview → risks of shifting the potential burdens
  - between different life cycle stages or individual processes
  - between different environmental impacts can be recognized and possibly avoided
- Sustainability of a product can be ensured already in the product development phase (Eco Design)

CCU LCA challenges

- No standartised way to carry out CCU LCA studies
- Asssessment results of the same CCU technology don’t match due to lack of standartisation, hence the transparency in the methodological choices
  - Makes hard to compare ’apples-to-apples’
- Comparison of the CCU technology to traditional one, the role of system boundary, multi-functionality and the system expansion
- Low TRL and its effect on the assesment and its results

Low TRL technologies

- Identification of the low TRL technologies
  - Technology maturity level affects the study's scope and goal, the questions that can be answered; data availability and study limitations.
  - The maturity of the product system shall equal the lowest maturity of the system elements / unit processes.
- For low TRL processes, studies are most useful for **hot spot analysis**. However, a comparison between a low TRL CCU technology and a high TRL reference technology can still reveal valuable insights to guide research.

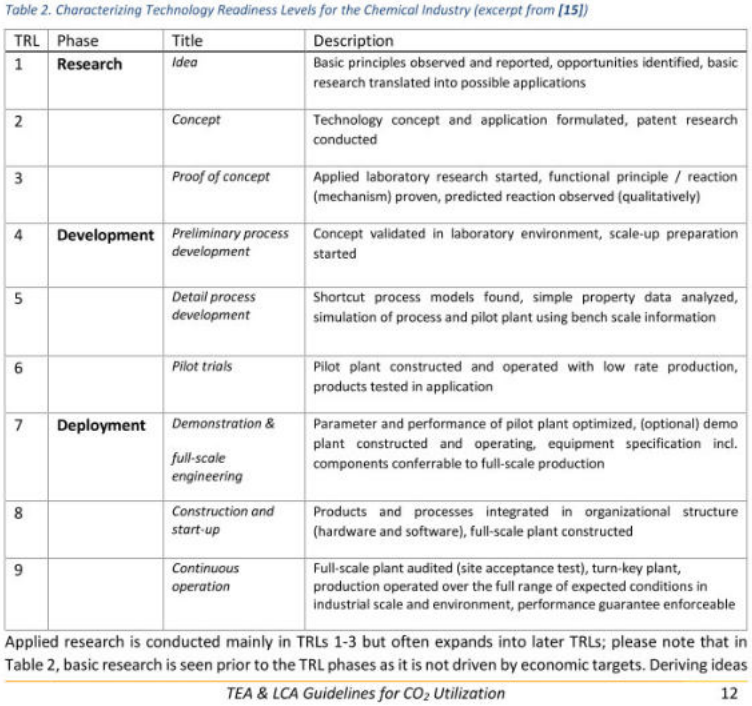


Table 2. Characterizing Technology Readiness Levels for the Chemical Industry (excerpt from ***[15]****)*

TRL	Phase	Title	Description
1	**Research**	*Idea*	Basic principles observed and reported, opportunities identified, basic research translated into possible applications
2		*Concept*	Technology concept and application formulated, patent research conducted
3		*Proof of concept*	Applied laboratory research started, functional principle / reaction (mechanism) proven, predicted reaction observed (qualitatively)
4	**Development**	*Preliminary process development*	Concept validated in laboratory environment, scale-up preparation started
5		*Detail process development*	Shortcut process models found, simple property data analyzed, simulation of process and pilot plant using bench scale information
6		*Pilot trials*	Pilot plant constructed and operated with low rate production, products tested in application
7	**Deployment**	*Demonstration &* *full-scale engineering*	Parameter and performance of pilot plant optimized, (optional) demo plant constructed and operating, equipment specification incl. components conferrable to full-scale production
8		*Construction and start-up*	Products and processes integrated in organizational structure (hardware and software), full-scale plant constructed
9		*Continuous operation*	Full-scale plant audited (site acceptance test), turn-key plant, production operated over the full range of expected conditions in industrial scale and environment, performance guarantee enforceable

Applied research is conducted mainly in TRLs 1-3 but often expands into later TRLs; please note that in Table 2, basic research is seen prior to the TRL phases as it is not driven by economic targets. Deriving ideas

TEA & LCA Guidelines for CO_2 Utilization 12

Emissions of the CCU system

The most crucial part is taking into account

- all CO_2 that is released into atmosphere and;
- understand impact on other environmental impact categories such as toxicity, acidification, fossils resource depletion
- thus, avoid shifting the burden from one category to another

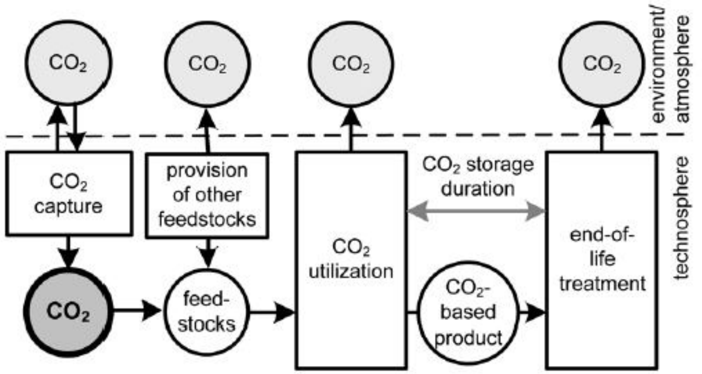
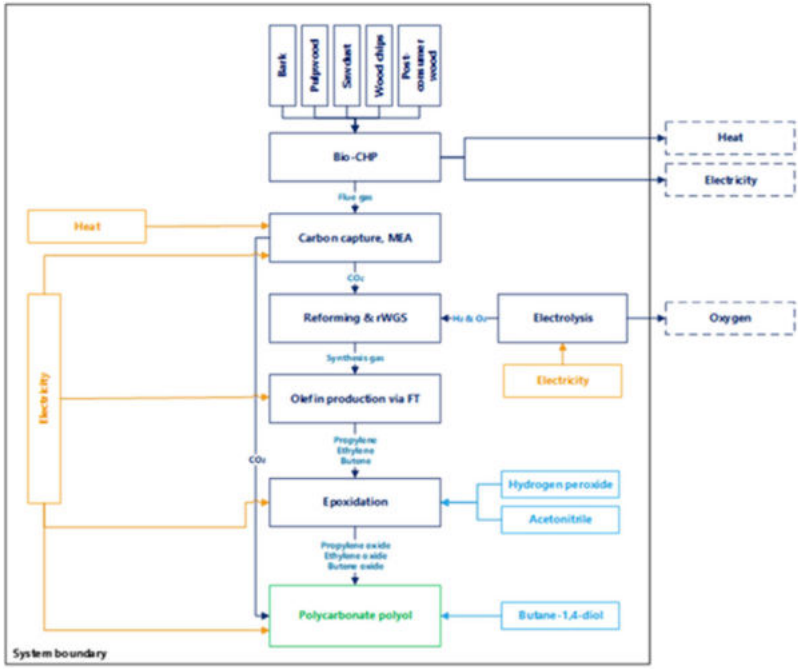


Fig. 1 The flow chart of the entire CCU system emphasizes the two subsystems of CO_2 capture and CO_2 utilization and classifies the feedstock CO_2 (in bold circle) as economic flow, not as negative emission.

(von der Assen et al. 2013)

The indirect emissions the CCU technologies

- The use of CCU technologies is not completely emission free due to its indirect emissions.
- The environmental impact results of the CCU products include the indirect emissions caused from the use of energy and other raw materials and substances in the process.
- The energy source used in the processes (e.g., natural gas energy, wind power, nuclear energy, solar energy), has a significant impact on the environmental performance of the whole concept under the assessment.



Classification of CO2 capture systems according to carbon origin

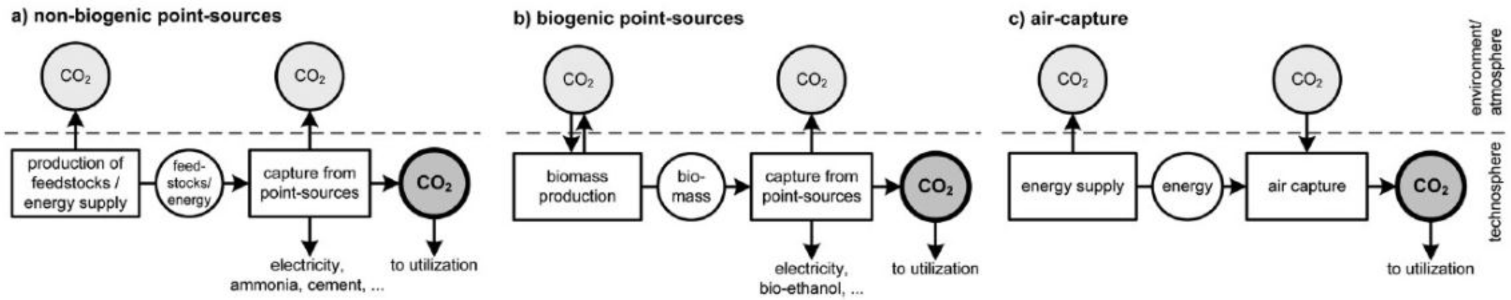


Fig. 2 Classification of CO_2 capture systems according to carbon origin: (a) CO_2 capture from non-biogenic point-sources includes capture from power plants and industrial processes; (b) CO_2 capture from biomass combustion or conversion processes and (c) CO_2 capture from ambient air. In cases of (a) and (b), a valuable product besides feedstock CO_2 is always co-produced. Only case (b) and (c) can potentially act as negative emission technologies.

(von der Assen et al. 2013)

Comparison of a CCU and conventional product

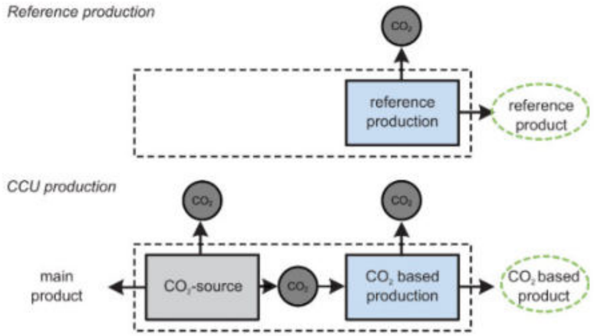


Figure 9: Comparison of a CCU production and a reference production: CCU system produces a main product besides CO_2-based product, i.e., the CCU system has additional functions not included in the functional unit (dashed green line). Thus, the conventional and CCU system are not comparable due to different functions.

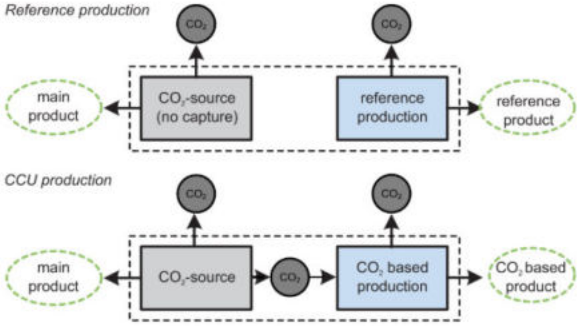


Figure 10: System expansion approach to compare a CCU production with a conventional production: the main product of CO_2-source is included in functional unit and the status-quo production system is expanded with the conventional production of the main product without carbon capture

CO_2 initiative, TEA & LCA guidelines for CO_2 utilization

- The Techno-Economic Assessment and Life Cycle Assessment Toolkit
- Techno-Economic Assessment & Life Cycle Assessment Guidelines for CO2 Utilization (Version 1.1) (Zimmerman et al. 2020)
  - Link to the document https://deepblue.lib.umich.edu/handle/2027.42/162573

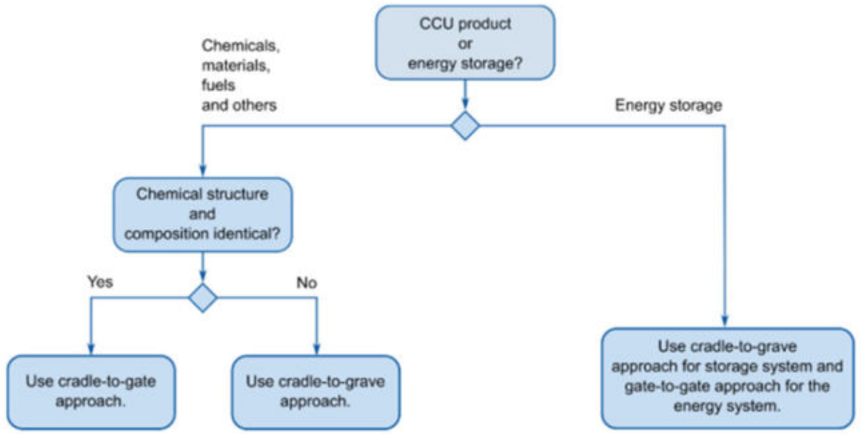


Figure 5: Decision tree for the selection of system boundaries

The potential of the CCU technologies in mitigating the climate change

The potential of the CCU technologies in mitigating the climate change

- the use of CO2 does not always reduce emissions or lead to net climate benefits, when the indirect and other effects of technology are considered
- CO2-based fuels and chemicals, can be classified as ‘cycling’. They circulate the carbon through industrial systems within timescales of days, weeks, months or, at best, decades.
- CO2 storage duration
  - The persistence of carbon storage varies from one CCU technology to another, where the storage time can range from a day to thousands of years.
  - The net climate impact of a CCU solution also depends to a large extent on the emission intensity of the applicable processes.
  - Mitigation measures require long-term storage of carbon dioxide, at least for centuries or thousands of years.
- The carbon cycle of short-term CCU applications should be closed to achieve net zero emissions, meaning that CO2 should be taken (as a resource) directly from the atmosphere by DAC (direct air capture) technologies or stored permanently by various means of land sequestration, such as photosynthesis) or by mineralization
  - The use of DAC involves a wide range of challenges, such as significant energy need, which must be zero-emission for the solution to have a mitigating effect on climate change
  - Permanent storage solutions have their own risks related to the release of carbon

The potential of the CCU technologies in mitigating the climate change

- Fast ‘cycling’ applications of the CO2 do not create the needed impact for mitigating the climate change but **enable reducing or completely avoiding the use of fossil resources, which would otherwise end up as emissions to atmosphere.**
- CCU technologies can lead **to reduction of overall production emissions, i.e., positive effects can be achieved beside the CO2 reduction also in other environmental impact categories** such as reduced acidification and eutrophication

Cradle-to-grave comparison based on CCU classification

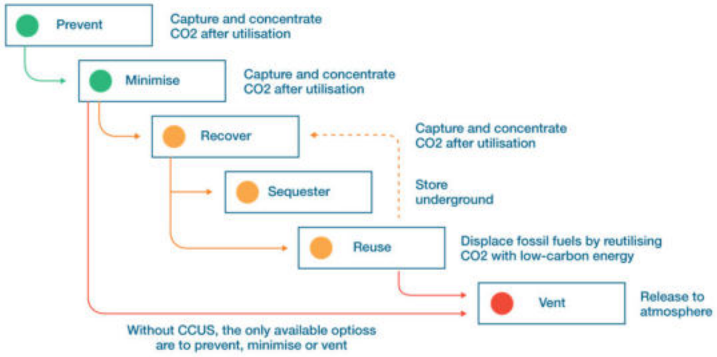
Figure 6: Comparison of environmental impacts for products with identical chemical structure and composition over the entire life cycle. Impacts only differ during raw material acquisition and production phases and thus, comparative studies only have to consider these phases.

(Zimmermann et al. 2018)

The potential of the CCU technologies in mitigating the climate change

- Carbon capture and use **(CCU) technologies have an enormous potential in reducing the environmental impacts and mitigating the climate change**, however applied alone, these technologies do not have the capacity to solve the climate crisis.
- From a climate change mitigation perspective, avoidance and reduction of the current emissions should be a priority, while simultaneously directing focus on developing solutions to current challenges for which **CCU and CCS technologies and their combination can be a tangible solution alongside other technologies.**

Fig 2. CCUS hierarchy by Hannula and Reiner (2017).



THANK YOU.

Vafa Järnefelt
vafa.jarnefelt@vtt.fi

#VTTbeyondtheobvious
#Circulareconomy

TAKE-OFF

Sustainable aviation fuel from CO_2

KEROGREEN

Take-Off

Production of synthetic renewable aviation fuel from CO_2, water and renewable electricity

Jan-Willem Könemann
KeroGreen Winter school 09-02-2022

TNO innovation for life

The TAKE-OFF “Production of synthetic renewable aviation fuel from CO_2 and H_2” project, that has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement N°101006799.

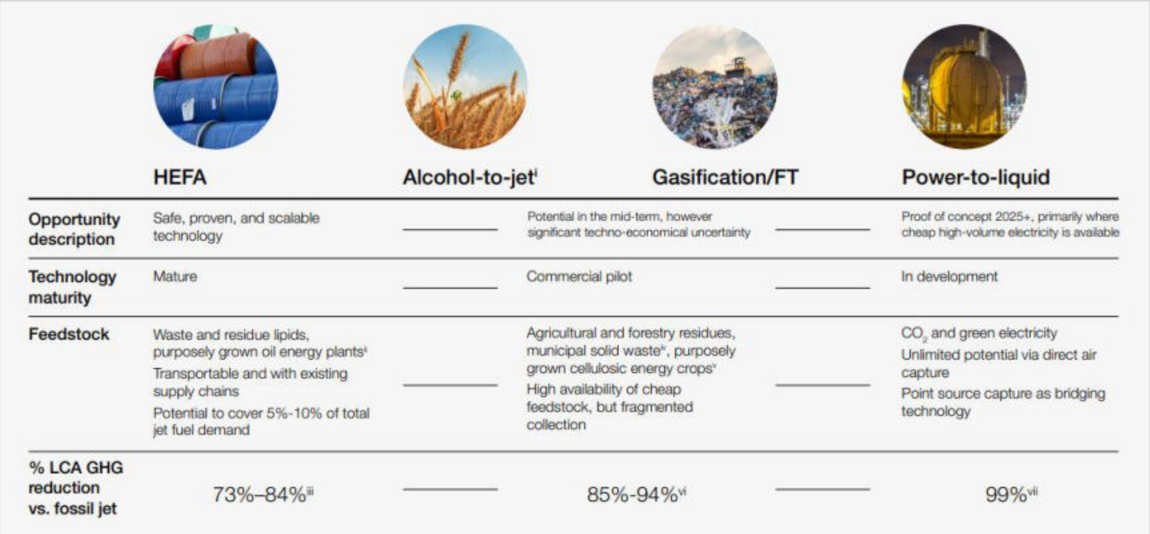
PUBLIC

Why Sustainable Aviation Fuels “SAF” ?

And why “synthetic” SAF?

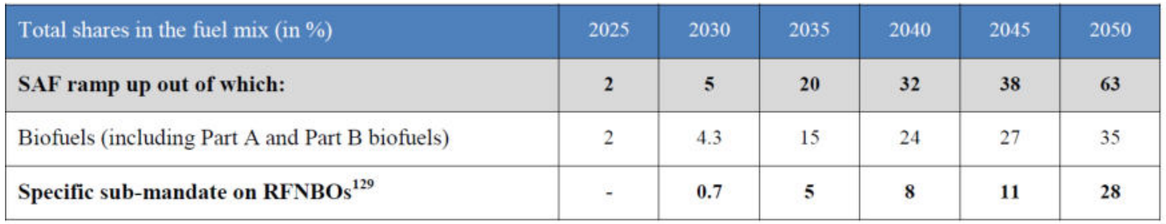
SAF, sustainable kerosene, is the only short to medium term possibility to make aviation sustainable.

- The kerosene market is huge, multiple technology routes will have to contribute
- Bio-kerosene is important and cheaper on short term, but is limited in feedstock
- Synthetic kerosene – produced from CO_2, H_2O and electricity - is currently still more expensive but has an unlimited feedstock
- Synthetic kerosene has the potential to reach near 100% green house gas reduction
- The importance of synthetic-SAF is underlined by governmental targets, incentives and market analysis
- Technology development is necessary to reduce costs



	HEFA	Alcohol-to-jet[i]	Gasification/FT	Power-to-liquid
Opportunity description	Safe, proven, and scalable technology		Potential in the mid-term, however significant techno-economical uncertainty	Proof of concept 2025+, primarily where cheap high-volume electricity is available
Technology maturity	Mature		Commercial pilot	In development
Feedstock	Waste and residue lipids, purposely grown oil energy plants[i] Transportable and with existing supply chains Potential to cover 5%-10% of total jet fuel demand		Agricultural and forestry residues, municipal solid waste[iv], purposely grown cellulosic energy crops[v] High availability of cheap feedstock, but fragmented collection	CO_2 and green electricity Unlimited potential via direct air capture Point source capture as bridging technology
% LCA GHG reduction vs. fossil jet	73%–84%[iii]		85%-94%[vi]	99%[vii]

Clean Skies for Tomorrow Sustainable Aviation Fuels as a Pathway to Net-Zero Aviation, November 2020, World Economic Forum in In Collaboration with McKinsey & Company https://www.mckinsey.com/industries/travel-logistics-and-infrastructure/our-insights/scaling-sustainable-aviation-fuel-today-for-clean-skies-tomorrow



Total shares in the fuel mix (in %)	2025	2030	2035	2040	2045	2050
SAF ramp up out of which:	**2**	**5**	**20**	**32**	**38**	**63**
Biofuels (including Part A and Part B biofuels)	2	4.3	15	24	27	35
Specific sub-mandate on RFNBOs[129]	**-**	**0.7**	**5**	**8**	**11**	**28**

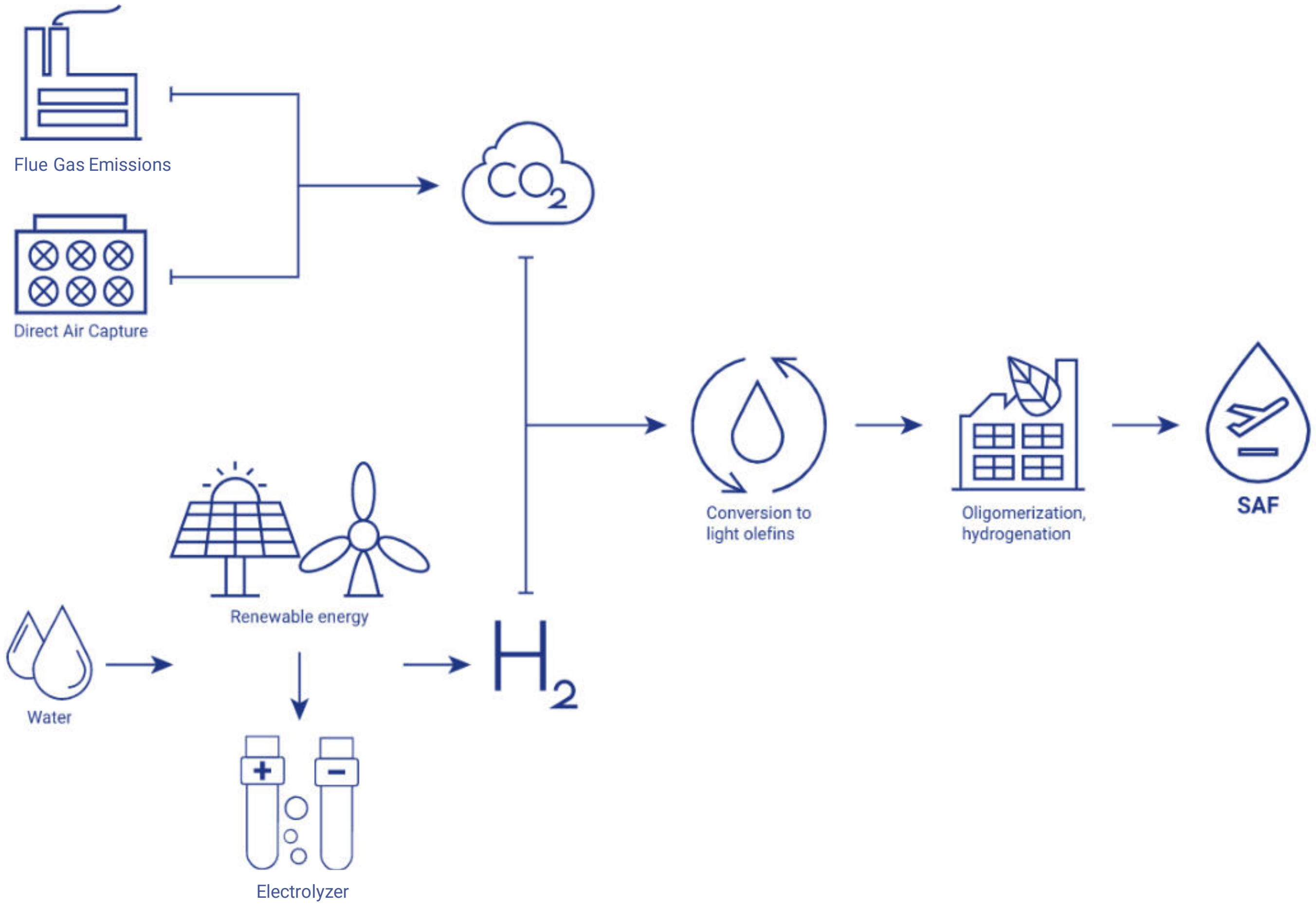
Proposal for a REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on ensuring a level playing field for sustainable air transport: https://ec.europa.eu/info/sites/default/files/refueleu_aviation_-_sustainable_aviation_fuels.pdf

Take-Off Technology Concept

Sustainable aviation fuel from CO_2, water and renewable electricity

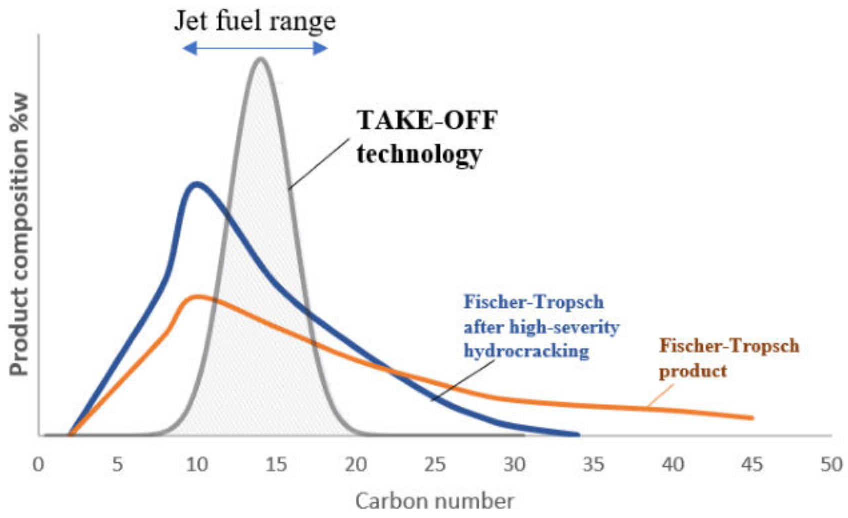
The TAKE-OFF project explores the development of a unique technology based on the conversion of CO_2, H_2O and renewable electricity to SAF via olefins as an intermediate.

- Innovative catalyst and reactor technologies are developed and demonstrated under industrially relevant conditions
- Objective is to significantly increase efficiency and reduce cost compared to the existing Power-to-Liquids benchmark

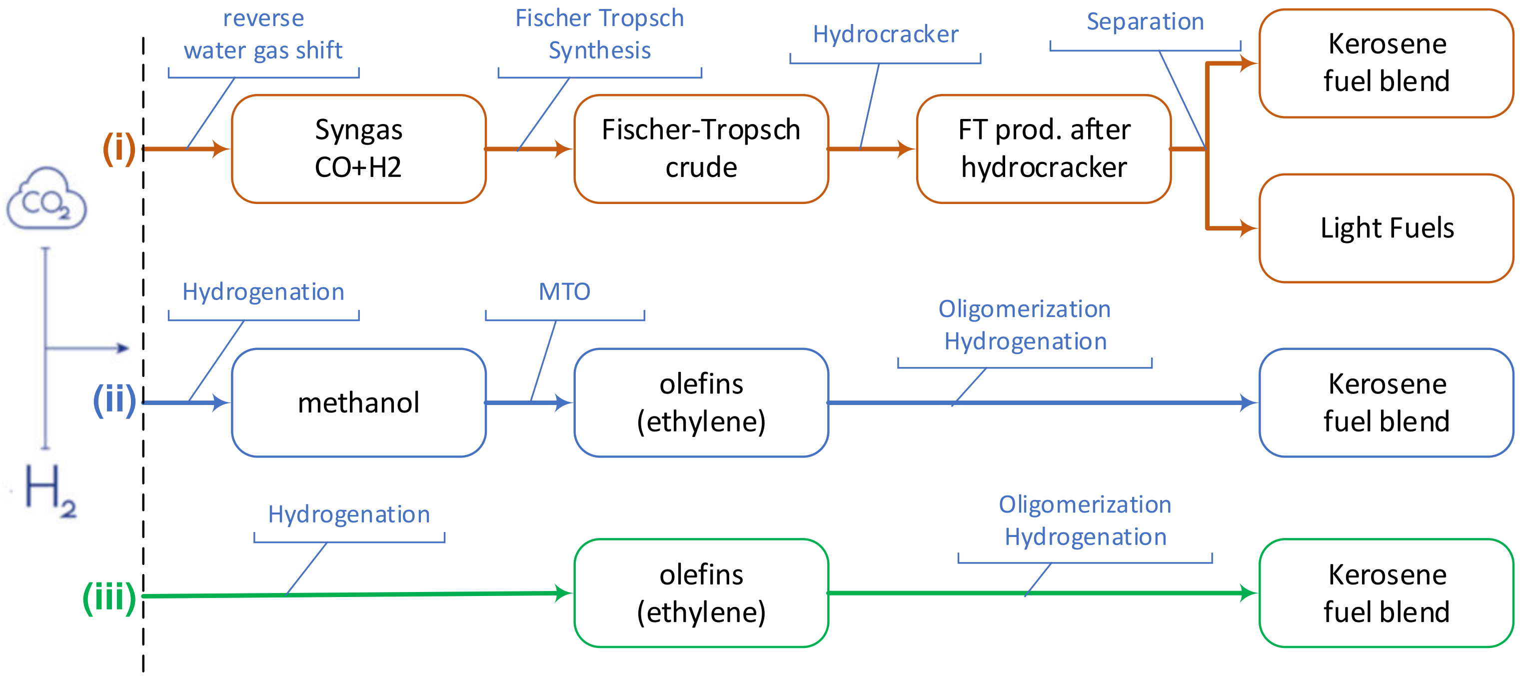


Take-Off route vs. the Fischer-Tropsch benchmark

The Fischer Tropsch route to kerosene is industrially proven at large scale and certified for use as aviation fuel. This route is therefore the industrial benchmark.



The main feature of the Take-Off route is that it is selective to the desired kerosene blend. Side products are avoided leading to a more selective use of H_2 towards the final kerosene end product


CO_2

H_2

(i) reverse water gas shift → Syngas CO+H2 → Fischer Tropsch Synthesis → Fischer-Tropsch crude → Hydrocracker → FT prod. after hydrocracker → Separation → Kerosene fuel blend / Light Fuels

(ii) Hydrogenation → methanol → MTO → olefins (ethylene) → Oligomerization Hydrogenation → Kerosene fuel blend

(iii) Hydrogenation → olefins (ethylene) → Oligomerization Hydrogenation → Kerosene fuel blend

Main steps in (i) Fischer Tropsch (ii) Take-Off via MeOH and (iii) Take-Off

Take-off consortium and advisory board

Partners shown at their main work package

Catalyst Development

cnrs

Reactor Technology

TNO
innovation
for life

Demonstration

RWE

MITSUBISHI
POWER

AsahiKASEI
ASAHI KASEI EUROPE

Compliance & emissions

FEV

RWTH AACHEN UNIVERSITY

SkyNRG

Techno-economic and environmental assessment

SDU
University of
Southern Denmark

Dissemination, Communication, Exploitation

CO₂ VALUE
EUROPE

Advisory Board

TotalEnergies

Global Alliance
POWERFUELS

NISA
Nordic Initiative for Sustainable Aviation

ExxonMobil

Port of
Amsterdam
Port of partnerships

KLM

dmt
Environmental
Technology

alcoenergy
sustainable pioneers | Rotterdam

Expected impact of the Take-Off project

- Advance the development of processes for the conversion of CO_2 to methanol, dimethyl ether (DME) and light olefins (ethylene) from TRL-3 to TRL-5. These intermediate products to the SAF end product have their own markets
- Advance an innovative olefins to jet fuel process from TRL-3 to TRL-4 and investigate compliance and emissions of the produced SAF
- Demonstrate the entire technology chain for Take-Off's next generation jet fuel technology
- Techno-economic and environmental assessments to support Take-Off's claims on efficiency, sustainability and costs reduction

+25%
Carbon and hydrogen efficiency
compared to other PtL alternatives

-100%
Sulphur
compared to fossil aviation fuel

-20%
Total emissions compared to
other PtL alternatives

-36%
SAF production costs
compared to other PtL alternatives

Stay in Touch with Take-Off

Current communication and dissemination activities

- Official website launched: TAKE OFF – Sustainable Aviation Fuel from CO2 (takeoff-project.eu)
- Social media: https://www.linkedin.com/company/take-off-euproject
- Take-Off advisory board is open for relevant industry participants
- Dissemination activities via participation in several conferences, scientific papers, and stakeholders meetings

TAKE-OFF
Sustainable aviation fuel from CO_2

Jan-Willem Könemann
Jan-willem.konemann@tno.nl

Jan-Willem Konemann
Sr. Business Developer - Energy Transition in Industry at TNO

The TAKE-OFF “Production of synthetic renewable aviation fuel from CO_2 and H_2” project, that has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement N°101006799.

E-fuel and BECCU projects

Research Professor Juha Lehtonen, VTT

09/02/2022 VTT – beyond the obvious

VTT Key Competences – Green Hydrogen and Power-to-X

Cutting-edge professionals

- 50 persons in hydrogen (production, storage and fuel cells)
- 30 persons in e-fuels synthesis & catalysis
- 30 persons in fuel testing and emissions
- 20 persons in TEA

Diverse reserach infrastructure

- E-fuels pilot (Mobile Synthesis Unit)
- Catalyst laboratories
- Engine lab for fuel and engine test
- Fuel cells and electrolyzers
- 5G pilot networks in order

Established networks

- Business Finland, ministries and EU as public sector networks
- Leading industry companies and NGOs as private sector partners
- Universities and research organizations as R&D partners

Broad IPR portfolio

- Hydrogen
  - 8 patents on electrolysis and fuel cells
- Synthesis
  - 15 patents on gas cleaning, catalysts, C1 reactions and CCU

E-fuel

Business Finland co-innovation project

Challenge

Efficient and profitable production of drop-in transportation fuels by Power-to-X

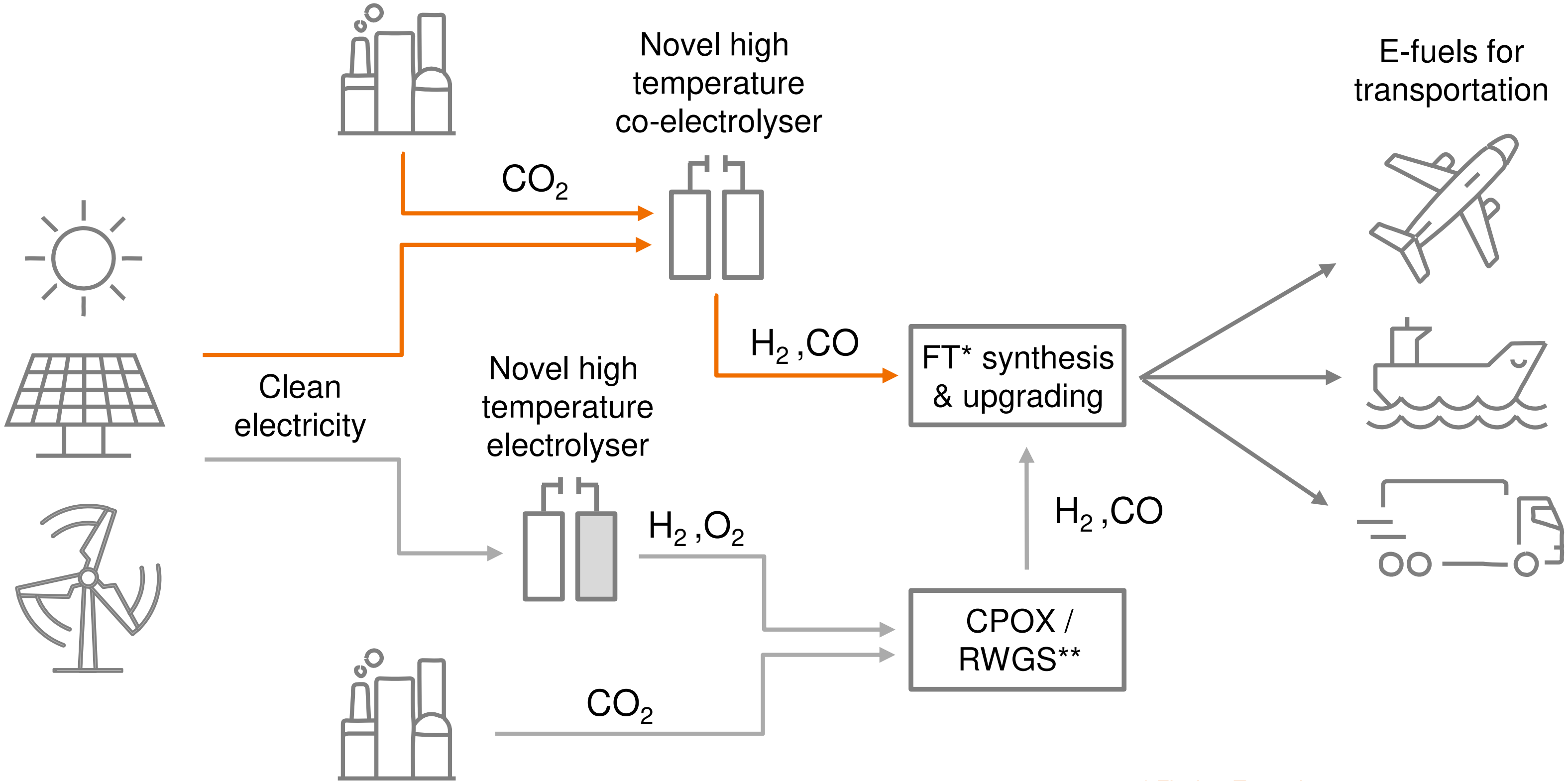
Our proposed solution

Combining of high temperature electrolysis and Fischer-Tropsch synthesis to obtain drop-in paraffinic fuels with high efficiency

Our vision

Year 2050, e-fuels will cover 20-30 % of final energy demand in transportation in Europe

E-fuel concept



* Fischer-Tropsch
**Catalytic partial oxidation / Reverse water-gas shift

The main objectives

1) To demonstrate production of drop-in paraffinic e-fuels in bench scale with high efficiency by combining and integrating high temperature electrolysis and Fischer-Tropsch synthesis
2) A readiness to scale up the concept after 2-year project to a production scale of 10 kton/a

Specific objectives

1. Development of thermal integration of solid oxide electrolysis cell (SOEC)
2. Development of catalytic partial oxidation (CPOX)/reverse water-gas shift (RWGS) concept integration
3. Development of integrated concept of CO_2 capture, electrolysis and FT synthesis
4. Demonstration of integrated concept in bench scale (>1000 hrs)
5. Demonstration of drop-in paraffinic e-fuel production (up to 300 kg) and usability
6. Ensuring the environmental and other impacts of produced paraffinic e-fuel

Project structure and external collaborations

VTT

Duration 1.1.2021 – 31.12.2022

Budget 3.3 M€

INTERNATIONAL

CO₂ VALUE EUROPE

FCH FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

ETIP Bioenergy European Technology and Innovation Platform

IEA Bioenergy Technology Collaboration Programme

Hydrogen Europe

FH

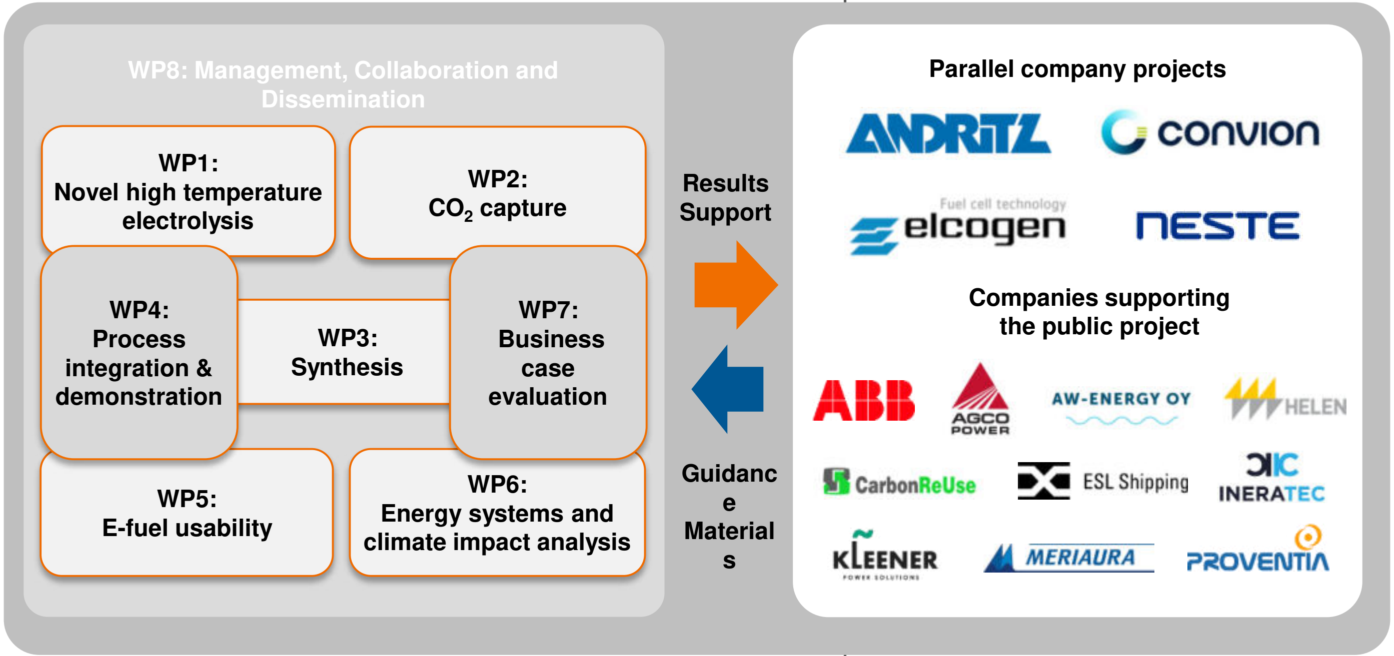
JÜLICH Forschungszentrum

KIT Karlsruhe Institute of Technology

LAT LABORATORY OF APPLIED THERMODYNAMICS

ieaghg

CERTH CENTRE FOR RESEARCH & TECHNOLOGY HELLAS



WP8: Management, Collaboration and Dissemination

WP1:
Novel high temperature electrolysis

WP2:
CO_2 capture

WP4:
Process integration & demonstration

WP3:
Synthesis

WP7:
Business case evaluation

WP5:
E-fuel usability

WP6:
Energy systems and climate impact analysis

Results Support

Guidance Material s

Parallel company projects

ANDRITZ

convion

elcogen Fuel cell technology

NESTE

Companies supporting the public project

ABB

AGCO POWER

AW-ENERGY OY

HELEN

CarbonReUse

ESL Shipping

INERATEC

KLEENER POWER SOLUTIONS

MERIAURA

PROVENTIA

NATIONAL

LUT University

BECCU

DECARBONATE

SYNC

ILMATIETEEN LAITOS

Tampere University

E-fuel demonstration – Integration of 3 units

Renewable electricity

Convion SOEC with Elcogen stacks

Industrial CO_2 emissions

CarbonReUse or Kleener CO_2 capture

VTT Mobsu

E-fuels for testing

E-fuel demonstration – VTT Bioruukki piloting centre

- 🟧 MOBSU
- 🟦 ELECTROLYSIS
- 🟩 H2 COMPR.
- 🟦 GAS CONTAINER
- 🟨 CO2 SEPARATION
- 🟥 CO2 COMPR.
- ○ STEAM/FLUE GAS

VTT

bio-energy

BECCU

based CO_2

for polyols

and fuels

Performance chemicals and transportation fuels from bio-CO_2 and hydrogen

Main objectives of the BECCU project

- Perform proof-of-concept for the integrated production of power & heat, specialty chemicals and transportation fuels based on utilization of CO_2 from bio-based operations and hydrogen from water electrolysis or industrial processes.

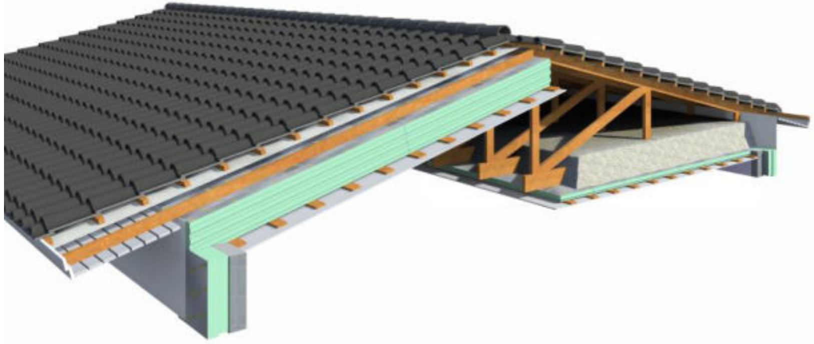
- Increase technical readiness levels (TRL) of the studied unit processes and develop the profitability of the concepts.

- Compare selected CO_2 utilization concepts (e.g. SNG, methanol) in contrast to CO_2 - based polyol products.

- Create new business opportunities throughout the value chain.

Versatile polyurethanes in the spotlight

- Target chemical products in BECCU project are polyols, including polycarbonate and polyether polyols, being important raw materials for polyurethanes.
- Polyurethanes are used as either flexible or rigid foams (to be used in insulation materials, footwear, automotive parts etc.) and as adhesives (for such applications as woodworking glues and in abrasive papers).



Polyurethane can be used in various long lifetime applications such as insulation materials
Figure: Finnfoam

Polyurethanes are widely used in adhesives for such applications as woodworking glues
Figure: Kiilto

The BECCU consortium

Parallel Business Finland company projects:

Valmet FORWARD
TOP ANALYTICA www.topanalytica.com
METENER
FINNFOAM

Other funding partner companies benefiting from the project:

KiiLTO
MIRKA
PIRKANMAAN JÄTEHUOLTO
CarbonReUse
NESTE
HELEN
KEMIANTEOLLISUUS
KLEENER POWER SOLUTIONS
Brightplus

International co-operation:

BERKELEY LAB Bringing Science Solutions to the World
M GLOBAL CO₂ INITIATIVE UNIVERSITY OF MICHIGAN
KIT Karlsruher Institut für Technologie
CO₂ VALUE EUROPE
nova
Perstorp

Main finance from Business Finland as part of **Green Electrification-ecosystem**

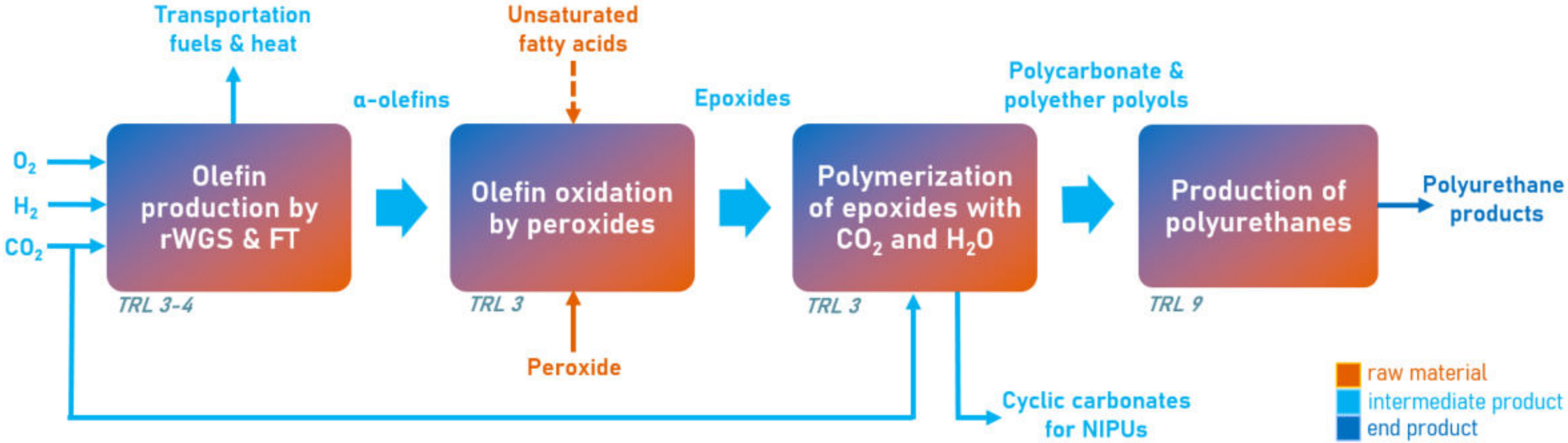
VTT's budget: 2.04 MEUR (co-innovation in total 4.84 MEUR)

Schedule: Jan/2020 – Aug/2022

BUSINESS FINLAND

Route for chemicals and polymers

- The process is based on the **production of olefins** through reverse water-gas shift (rWGS) and Fischer-Tropsch (FT) reaction steps.
- The olefins are further converted to epoxides through oxidation reactions by peroxides and epoxides are polymerized together with CO_2 to obtain polyols.
- The yield of C2-C4 olefins is maximized to be used in polyol production and higher hydrocarbons are utilized as energy carriers (waxes or fuels).



O_2

H_2

CO_2

Olefin production by rWGS & FT

TRL 3-4

Transportation fuels & heat

α-olefins

Unsaturated fatty acids

Olefin oxidation by peroxides

TRL 3

Peroxide

Epoxides

Polymerization of epoxides with CO_2 and H_2O

TRL 3

Cyclic carbonates for NIPUs

Polycarbonate & polyether polyols

Production of polyurethanes

TRL 9

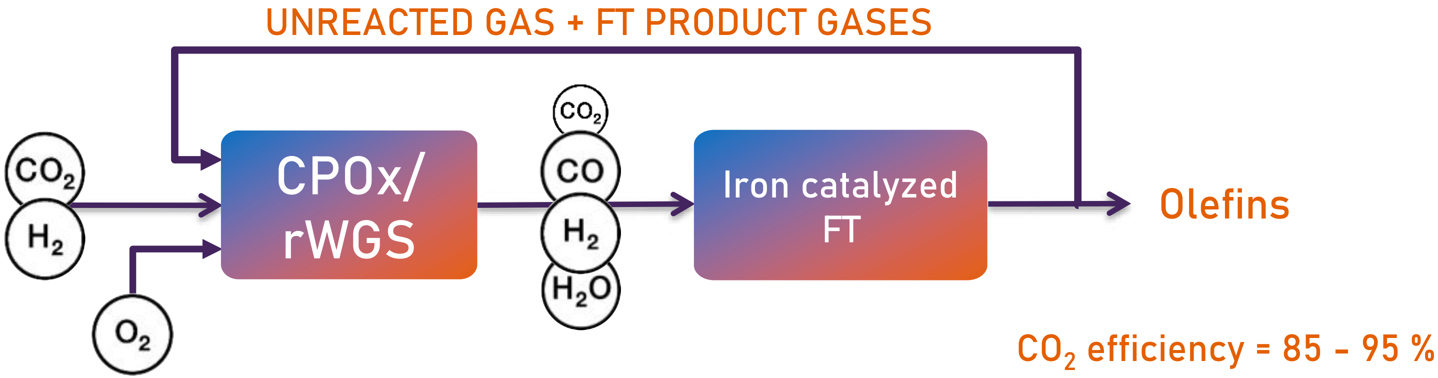
Polyurethane products

🟧 raw material

🟦 intermediate product

🟦 end product

Enhanced carbon efficiency by the circulation of methane and unreacted gases in Fischer-Tropsch



CO_2 efficiency = 85 - 95 %

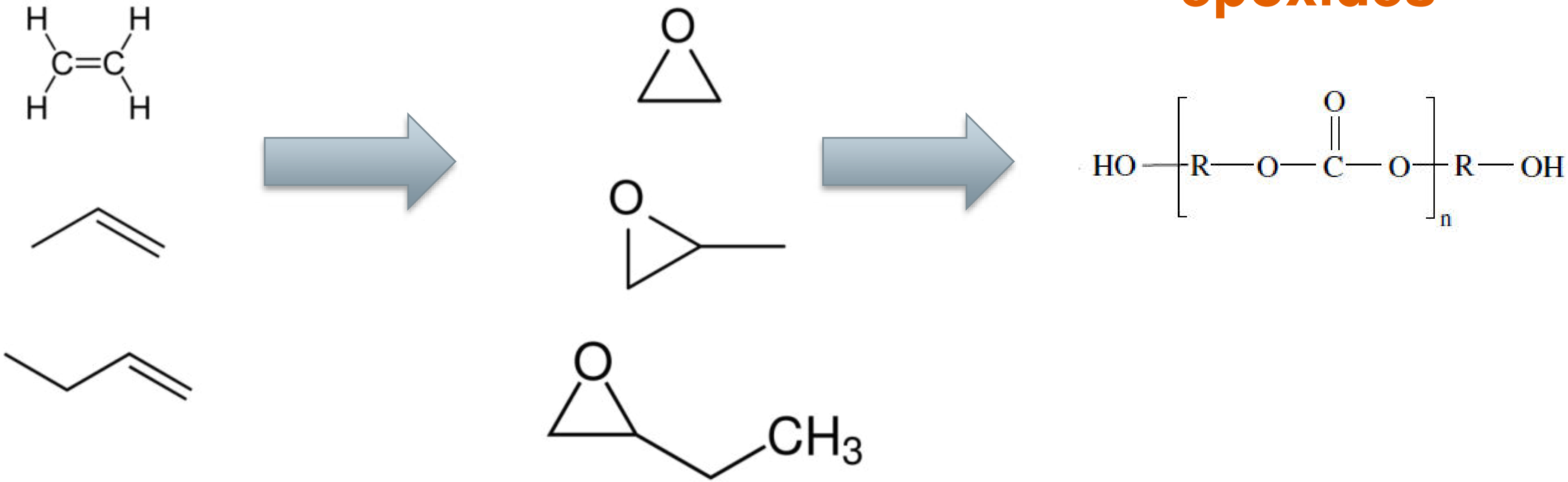
CPOx: Catalytic partial oxidation

Polyols from mixed C2-C4 olefins

Mixed olefins

Mixed epoxides

Polyols from mixed epoxides



Polycarbonate polyol synthesis

- PO and BO copolymerization with CO_2
  - Heterogeneous and homogeneous catalysts applied
  - Varying Mw of the product by changing process conditions and starter polyol concentration
  - Application tests for polyurethane formulations starting

Products based on BO

Products based on PO

beyond

the obvious

CO_2 supply for P2X: *Carbon capture research in VTT's BECCU and E-Fuel projects*

KEROGREEN Winter School, 10.–11.2.2022, online

Onni Linjala, Research Scientist (MSc),
VTT Technical Research Centre of Finland

10.2.2022 VTT – beyond the obvious

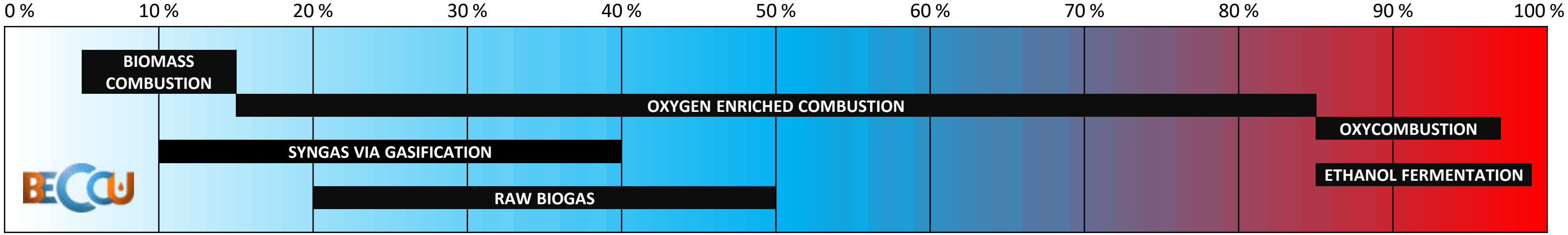
CO_2 supply via carbon capture

We examine carbon capture from the emission streams of energy sector and industry to provide CO_2 supply for P2X. We focus on **post-combustion capture** and **inherent capture** over direct air capture due to better economics and higher technological maturity.

- Bioenergy (CHP, forest industry)
- Biorefineries (biogas, HVO, bioethanol)

- Forest industry: high potential for bio-CCUS
- Bio- and petroleum refineries: many high CO_2 concentration emission streams with potential for low CO_2 capture costs

CO_2 vol-% (in dry gas)



Factors for carbon capture technology choice

Emission source characterization

- Capacity, biogenic vs. fossil, feed gas composition (CO_2 concentration, impurities), temperature, pressure

System integration

- Availability of energy streams: steam, low-grade heat, electricity, cooling
- Equipment size restrictions
- Emission and waste stream control, other utility needs

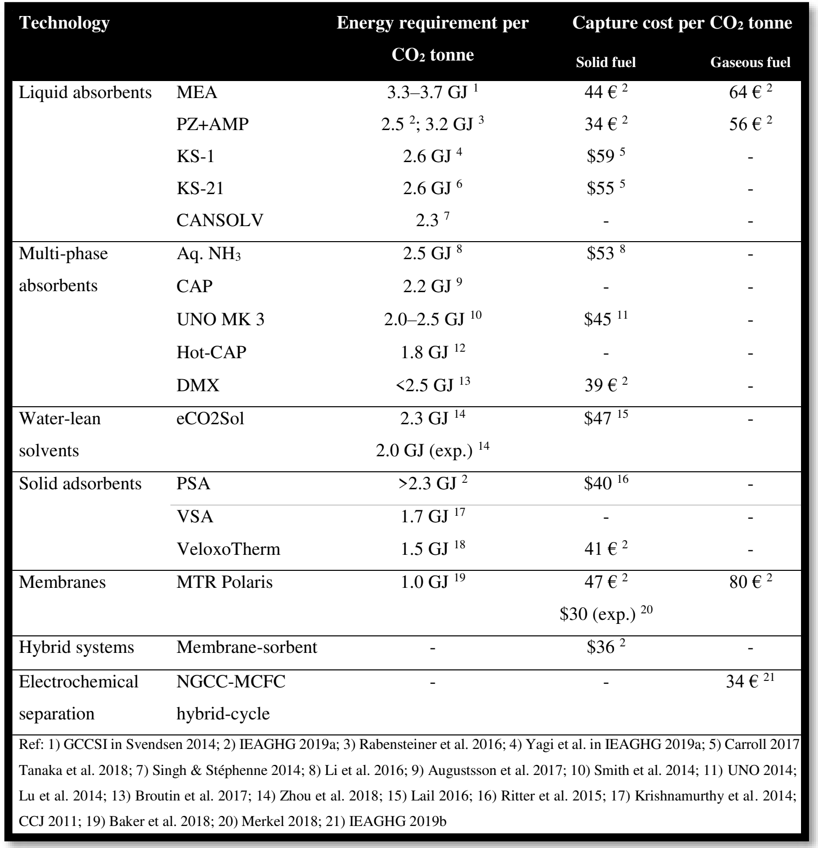
Desired capture properties

- CO_2 quality (determined by transportation and end-use application)
- Capture efficiency (harmful fossil-CO_2 vs. neutral bio-CO_2)

Literature review on post-combustion capture technologies

- Numerous technologies based on different phenomena are available and in development, e.g., liquid solvents, solid sorbents, membranes and fuel cell systems.
- No clear breakthrough technologies regarding performance, but amine-based solvents have a distinct lead in maturity.
- Commercial-scale operation is ongoing with amines mainly in fossil-CCS applications. Many demonstration/scale-up projects upcoming for other emerging technologies.
- Capture costs are decreasing as technologies advance. Currently, approaching a capture cost of 30 €/tCO_2 in post-combustion capture applications.

Capture cost in post combustion capture:
- All the reviewed technologies: 34–80 €/tCO_2
- On average: 40–60 €/tCO_2



Technology		Energy requirement per CO_2 tonne	Capture cost per CO_2 tonne	
			Solid fuel	Gaseous fuel
Liquid absorbents	MEA	3.3–3.7 GJ [1]	44 € [2]	64 € [2]
	PZ+AMP	2.5 [2]; 3.2 GJ [3]	34 € [2]	56 € [2]
	KS-1	2.6 GJ [4]	$59 [5]	-
	KS-21	2.6 GJ [6]	$55 [5]	-
	CANSOLV	2.3 [7]	-	-
Multi-phase absorbents	Aq. NH_3	2.5 GJ [8]	$53 [8]	-
	CAP	2.2 GJ [9]	-	-
	UNO MK 3	2.0–2.5 GJ [10]	$45 [11]	-
	Hot-CAP	1.8 GJ [12]	-	-
	DMX	<2.5 GJ [13]	39 € [2]	-
Water-lean solvents	eCO2Sol	2.3 GJ [14] 2.0 GJ (exp.) [14]	$47 [15]	-
Solid adsorbents	PSA	>2.3 GJ [2]	$40 [16]	-
	VSA	1.7 GJ [17]	-	-
	VeloxoTherm	1.5 GJ [18]	41 € [2]	-
Membranes	MTR Polaris	1.0 GJ [19]	47 € [2] $30 (exp.) [20]	80 € [2]
Hybrid systems	Membrane-sorbent	-	$36 [2]	-
Electrochemical separation	NGCC-MCFC hybrid-cycle	-	-	34 € [21]

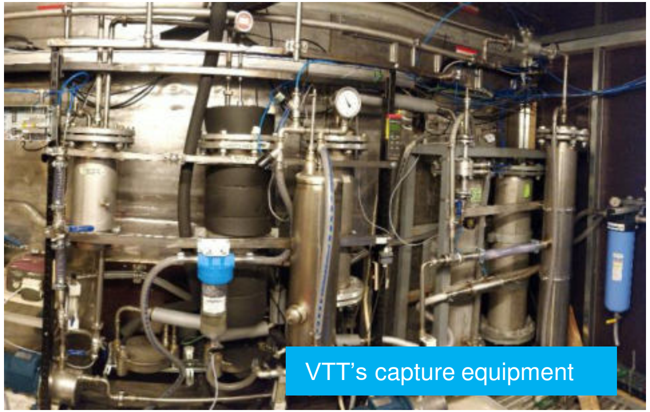
Ref: 1) GCCSI in Svendsen 2014; 2) IEAGHG 2019a; 3) Rabensteiner et al. 2016; 4) Yagi et al. in IEAGHG 2019a; 5) Carroll 2017 Tanaka et al. 2018; 7) Singh & Stéphenne 2014; 8) Li et al. 2016; 9) Augustsson et al. 2017; 10) Smith et al. 2014; 11) UNO 2014; Lu et al. 2014; 13) Broutin et al. 2017; 14) Zhou et al. 2018; 15) Lail 2016; 16) Ritter et al. 2015; 17) Krishnamurthy et al. 2014; CCJ 2011; 19) Baker et al. 2018; 20) Merkel 2018; 21) IEAGHG 2019b

Available: Review on post-combustion carbon capture technologies and capture of biogenic CO_2 using pilot-scale equipment

Carbon capture tested at TRL 5–6 in BECCU

- **Three novel post-combustion capture technologies** were tested with synthetic gas mixtures, flue gases from biomass combustion (50 kW CFB-pilot), and biogas at Jyväskylä, Finland in September of 2020.
- **Objective of the test runs** was to verify proper function of the technologies in realistic conditions and to gather data on the effect of different operating conditions on the performance of the capture technologies. The test results are also utilized in process modeling.


Test site


VTT’s capture equipment

Three novel Finnish technologies tested in BECCU

Technology	Enhanced water scrubbing	Enhanced soda scrubbing	Kleener-liquid
Capture phenomenon	Physical absorption	Chemical absorption	Chemical absorption
Capture solvent	Water (no chemicals)	Aqueuos sodium carbonate solvent (Na_2CO_3)	A novel ash-based capture solvent
Absorber equipment	Bubble-type absorption column	VTT’s novel micro-bubble generator	VTT’s equipment used in BECCU tests
Absorption conditions	5 °C 4–5 bar	30–40 °C atm	50–65 °C atm
Regeneration conditions	Pressure flash ~0.4 bar	60–80 °C Vacuum 0.2–0.5 bar	60–80 °C Vacuum 0.2–0.5 bar
Required energy supply	Electricity	Low-grade heat for regeneration Electricity for auxiliaries	Low-grade heat for regeneration Electricity for auxiliaries

Promising results achieved at small pilot-scale

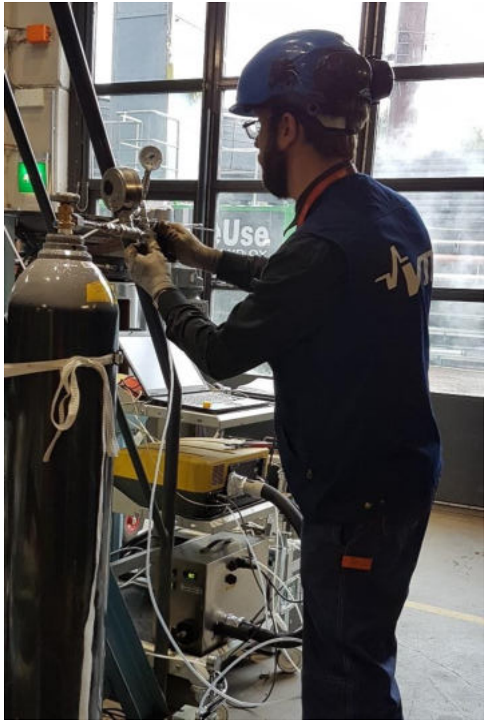
Purity of the captured CO_2 [mean vol-% in dry gas]

	CarbonReUse	Kleener*	VTT Soda
Synthetic gas 15 vol-% CO_2	95.1	-	96.7
Synthetic gas 30 vol-% CO_2	98.3	-	-
Pine chips (flue gas)	97.1	94.2	95.9
Washed straw (flue gas)	96.0	-	96.6
Spruce bark (flue gas)	-	-	96.5
Raw biogas	-	-	93.6

Capture efficiency [%]

	CarbonReUse	Kleener*	VTT Soda
Synthetic gas 15 vol-% CO_2	74	-	83–86
Synthetic gas 30 vol-% CO_2	86	-	-
Pine chips (flue gas)	72–76	69–71	74–79
Washed straw (flue gas)	64–70	-	78–83
Spruce bark (flue gas)	-	-	88-90
Raw biogas	-	-	97–98

*A diluted version of the Kleener-liquid (25 wt-%. solution vs. the ”normal” 50 wt-% solution) was tested in the BECCU test runs. Higher capture perfomance can be expected with the normal formula.



Conclusions and next steps

CONCLUSIONS

- A literature review was conducted to map carbon capture technology options and to evaluate techno-economic performance of the technologies.
- Three novel capture technologies were proven functional in post-combustion carbon capture at realistic conditions at TRL 5-6.
- Performance of the tested technologies are promising and in align with other carbon capture technologies at similar scale. Further work is required to evaluate economics of the capture processes at industrial-scale.

NEXT STEPS

- Process modelling and TEA for carbon capture.
- Carbon capture potential of forest industry and refinery processes are evaluated, and suitable capture technology options for these industries are assessed.
- As part of E-Fuel, carbon capture will be tested at a relevant industrial environment, with integration to SOEC high-temperature co-electrolysis and mobile FT synthesis unit for in-situ production of FT fuels.
- VTT’s enhaced soda scrubbing technology is further developed by enhancing mass transfer and energy efficiency. Also, scale-up options are assessed.

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VTT

Techno-economics of the synthesis route from CO_2 and clean H_2 to polycarbonate polyols

Miia Nevander
KEROGREEN Winter School
10.2.2022

BECCU

Agenda

Process route to polyols & background

Results from preliminary TEA of BECCU-polyols

Updated process simulation with Aspen Plus

Suggested improvements & conclusions

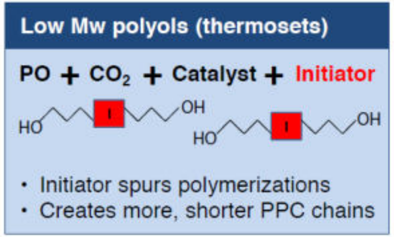
Discussion

VTT

Process route to polyols & background

10/02/2022 VTT – beyond the obvious

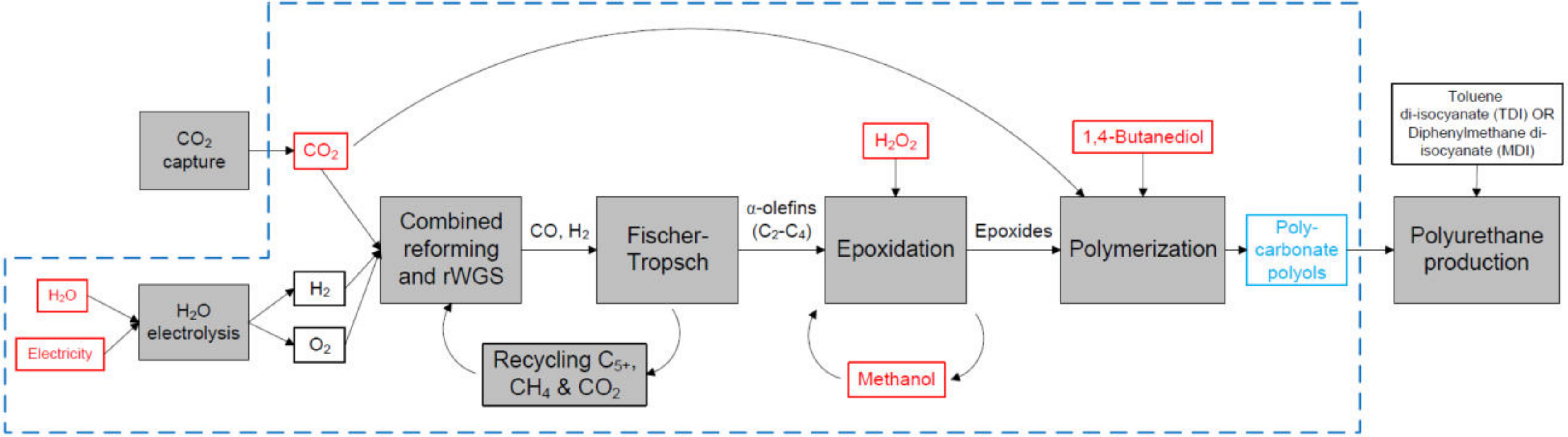
Polycarbonate polyols – high value chemicals and plastics

Term	Definition	Structural formula
Polycarbonate polyol	Low molecular weight polymer, linear aliphatic polycarbonate, derived from the copolymerization of carbon dioxide and an epoxide, containing two or more terminal hydroxyl groups (Qin & Wang, 2019)	 **Low Mw polyols (thermosets)** **PO + CO_2 + Catalyst + Initiator** • Initiator spurs polymerizations • Creates more, shorter PPC chains (Raschka et al., 2018)

- High value product, selling price can be even 6 000 €/tonne
- Applications: polyurethanes, coatings, adhesives, …

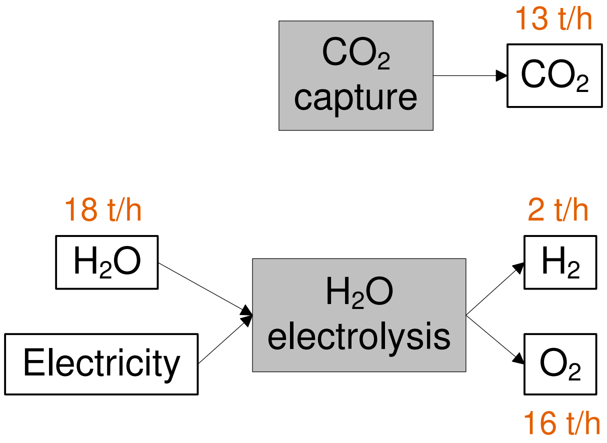
BECCU-polyols from biogenic CO_2 & green H_2

- The process is based on the **production of olefins** through reverse water-gas shift (rWGS) and Fischer-Tropsch (FT) reaction steps
- The olefins are further converted to epoxides through oxidation reactions by peroxides and epoxides are polymerized together with CO_2 to obtain polyols
- The yield of C_2-C_4 olefins is maximized to be used in polyol production



Carbon dioxide & hydrogen as starting materials

- CO_2 from biogenic sources with MEA
  - 50 €/tonne capture & processing cost assumed
- H_2 from alkaline electrolysis (AEC)
  - 100 MW electrolyser (η=67%)
  - 60 M€ electrolyser & costs of water and electricity



Results from preliminary TEA of BECCU-polyols

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Assumptions & results

Inputs	Price	Outputs	Price
Electricity (total)	**45 €/MWh**	**Cyclic carbonates**	**900 €/t**
Hydrogen peroxide	**550 €/t**	**By-product heat**	**20 €/MWh**
CO_2 supply	**50 €/t**	**By-product oxygen**	**40 €/t**

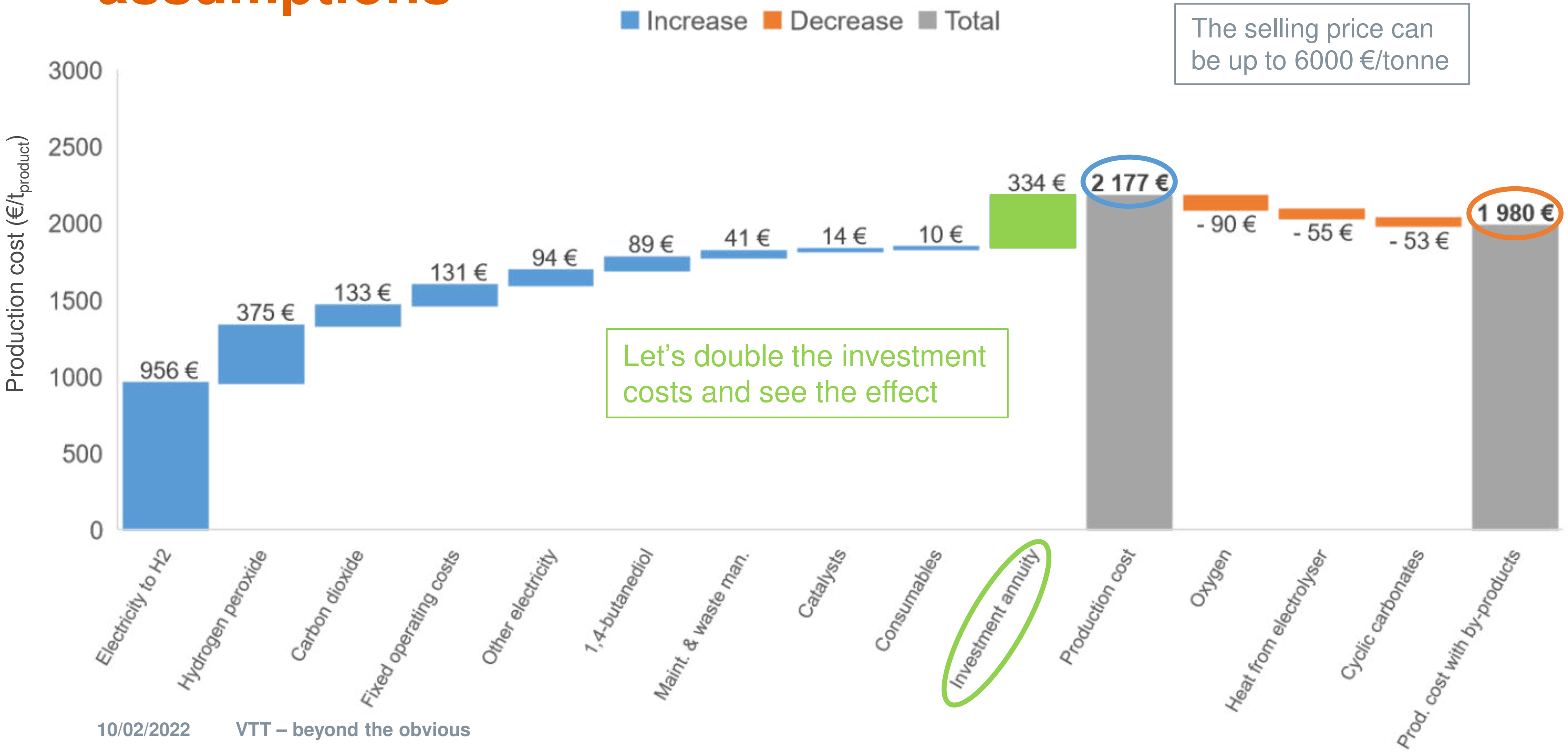
Other parameters	
Electrolyser electricity input	**100 MW_e**
Annual plant operation time	**8 000 h**
Total investment cost estimate ***(20 years and 8% WACC for annuity)***	**124 M€**

IN	
CO_2 need	100 kt/a
H_2 need	16 kt/a

→

OUT	
Polycarbonate polyols	38 kt/a
Cyclic carbonates	2 kt/a
Excess oxygen	84 kt/a

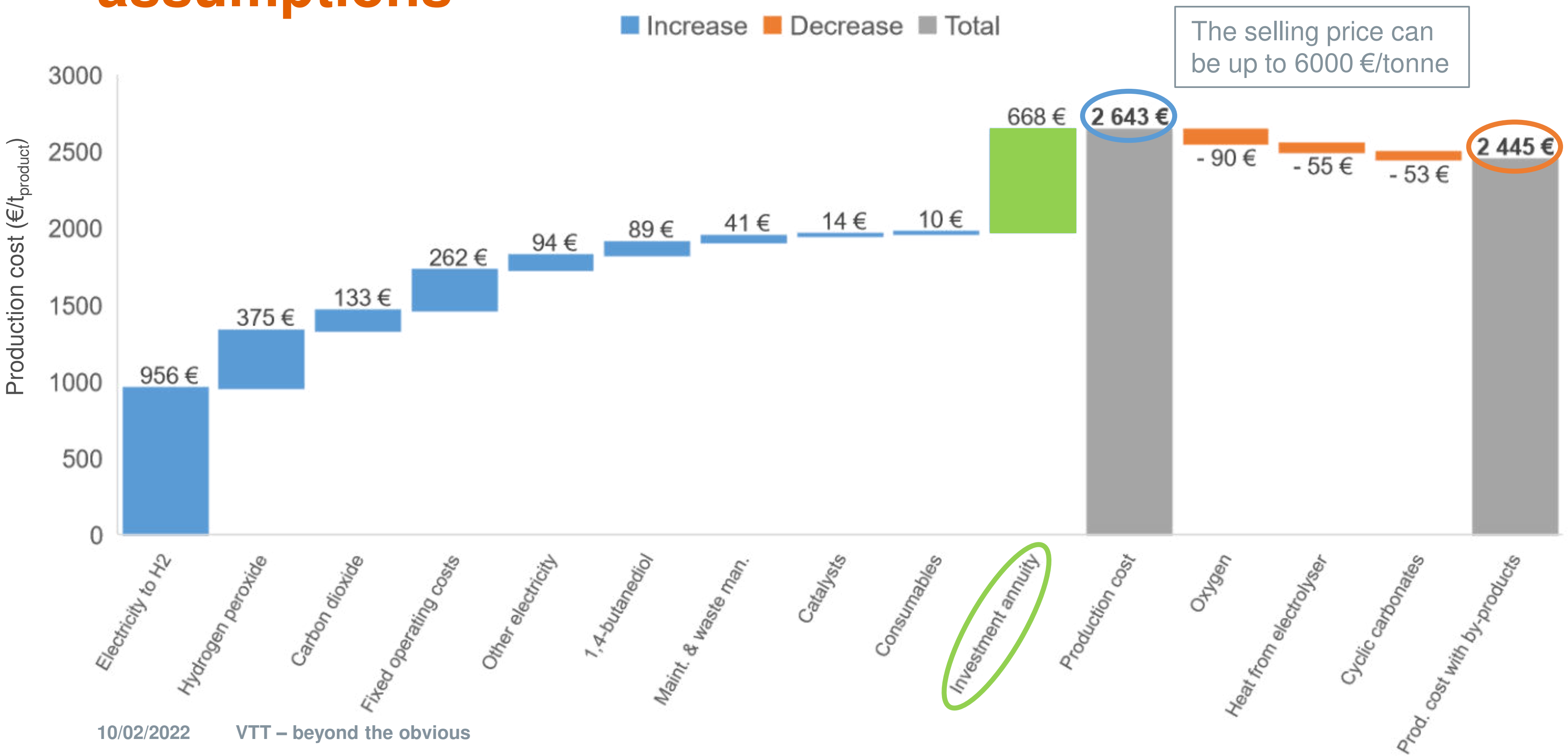
Production cost estimation with preliminary assumptions



The selling price can be up to 6000 €/tonne

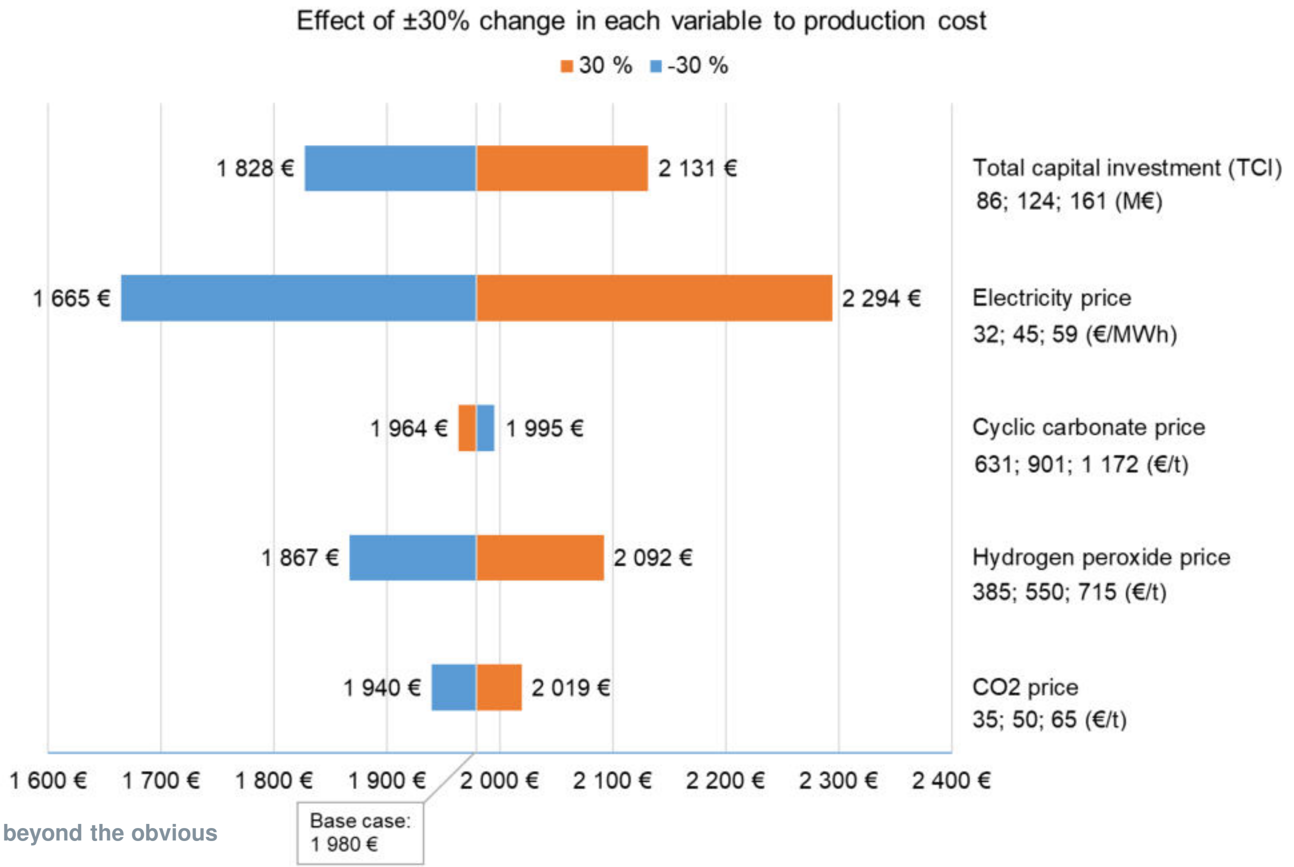
Let's double the investment costs and see the effect

Production cost estimation with preliminary assumptions



The selling price can be up to 6000 €/tonne

The production costs are heavily dependent on the price of electricity



Updated process simulation with Aspen Plus

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Simulation model improved since the preliminary TEA results

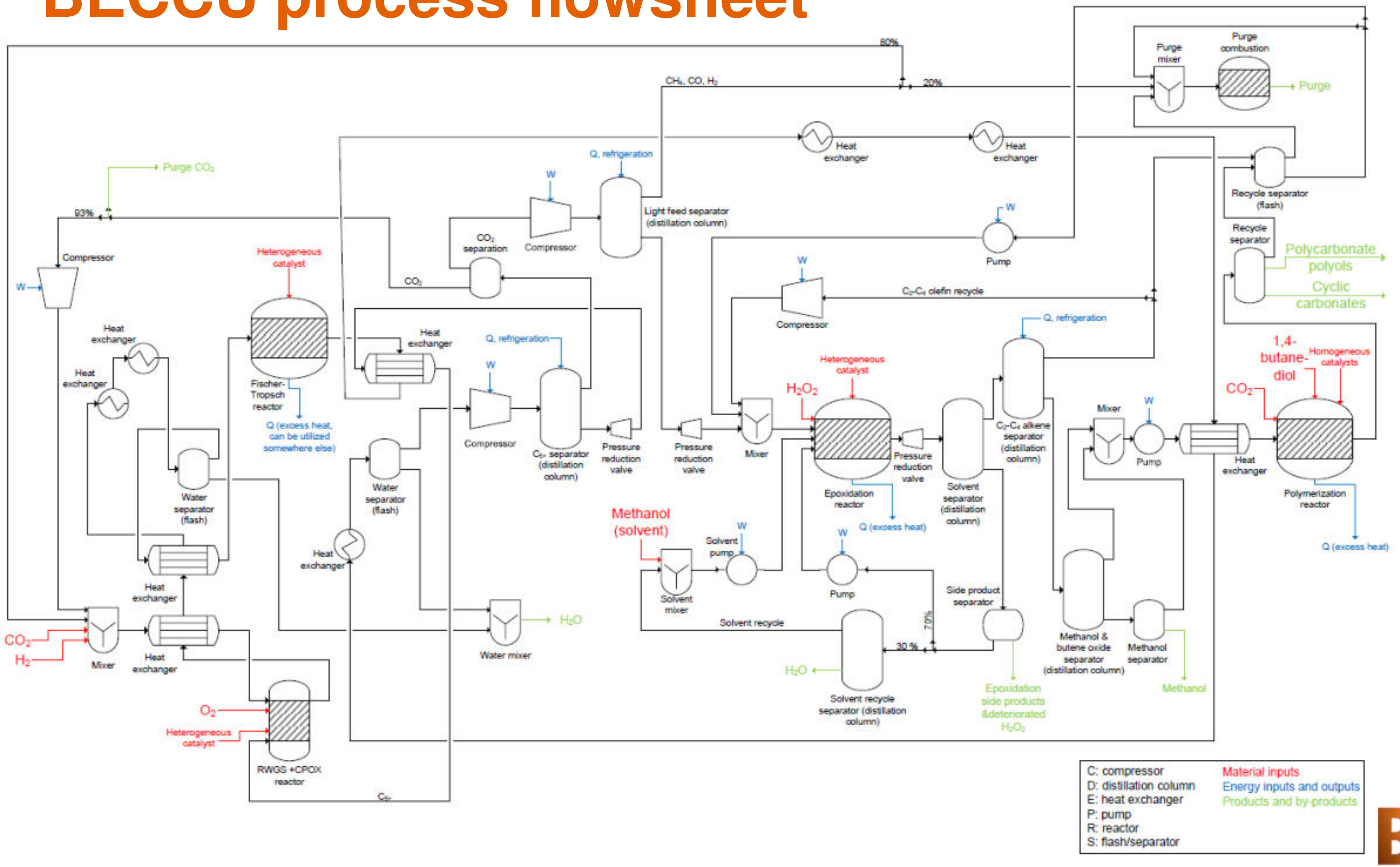
- Raw material in epoxidation, ethene, is difficult to separate from other light substances when there is CO_2 in the feed
  - CO_2 freezes in temperatures needed for cryogenic separation
  - ➢ We assume a separation method for CO_2 and are able to retrieve ethene to epoxidation

- Recycle loop added for epoxidation solvent (methanol)
  - Energy consumption of separations optimized

- Experimentally discovered side products have been added to the model

- Reactor performances have been revised and updated

BECCU process flowsheet



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Suggested improvements & conclusions

Room for improvements after BECCU project

Separation of CO_2 after Fischer-Tropsch (FT)

- FT catalyst is both rWGS and WGS active, so there should be some CO_2 in the feed to FT
- Further investigation needed to find the most suitable separation method

Separation of side products of epoxidation

- Side products form azeotropes with methanol, water and other components, so the separation seems challenging

Epoxidation solvent (methanol) and product (1-butene oxide) have boiling points very close to each other, and they form azeotropes

- Difficult to separate
- Liquid-liquid extraction process should be further investigated

The modelling of polycarbonate polyols

- Polymer modelling requires thermodynamic data
- The products are not added to Aspen model

Conclusions

- BECCU production route seems competitive & profitable
  - Production cost was found lower than the expected selling price
- Sensitivity analysis showed that the process is most sensitive to changes in electricity price
  - TCI and H_2O_2 price have the second and third greatest effect

➢ An improved TEA is in the making, with the updated process model and experimental findings

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10/02/2022

Questions & Discussion

KEROGREEN Winter School " Future directions in research on Power-to-X for sustainable chemicals & fuels", 10-11.02.2022, online

Process intensification for advancing Power-to-Fuels

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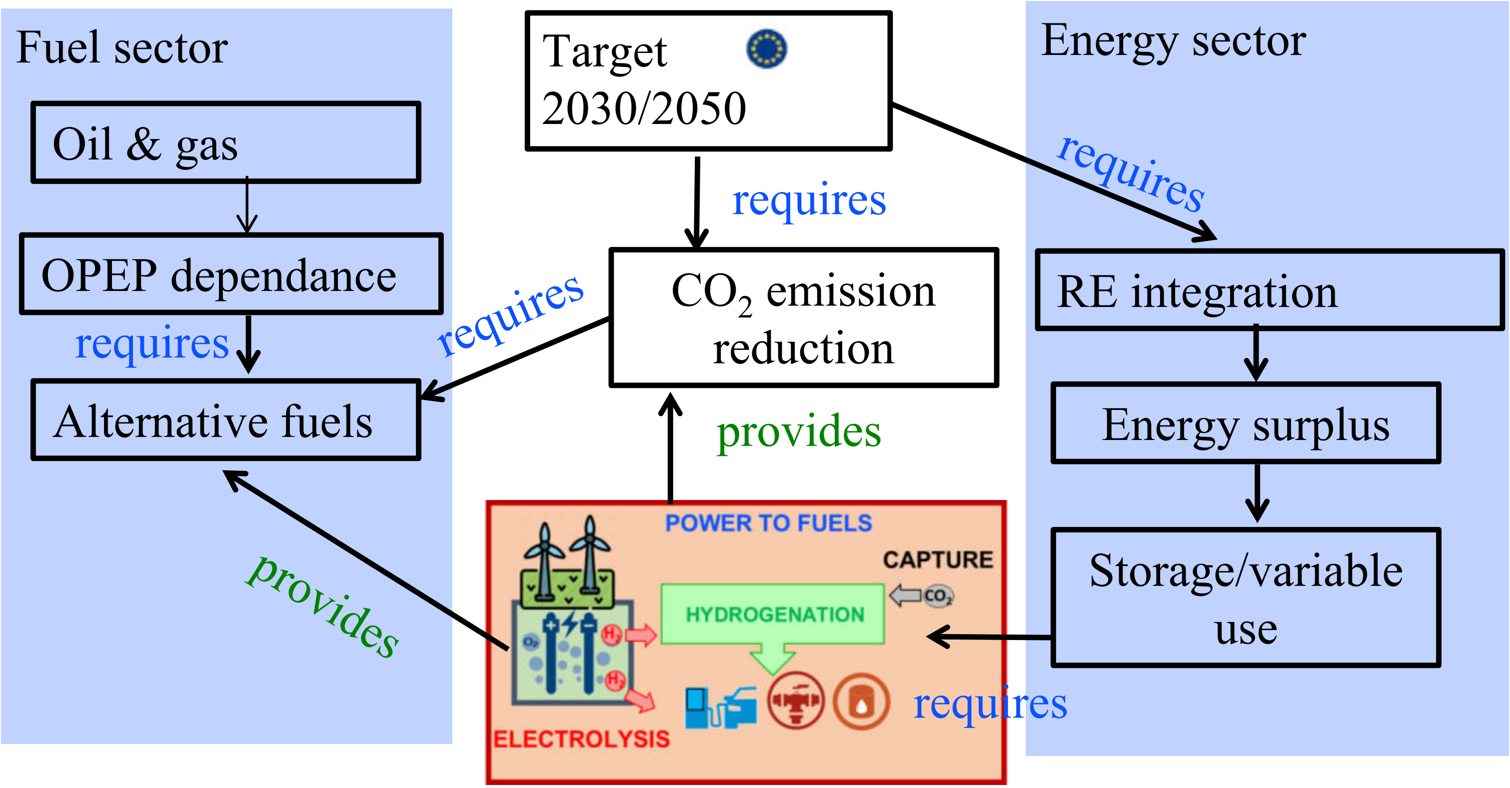
Web: http://rdgroups.ciemat.es/web/valer

Energy Department
CIEMAT

¿Why Power-to-Fuels?



Fuel sector

Oil & gas

OPEP dependance

requires

Alternative fuels

provides

Target 2030/2050

requires

CO_2 emission reduction

requires

provides

Energy sector

requires

RE integration

Energy surplus

Storage/variable use

requires

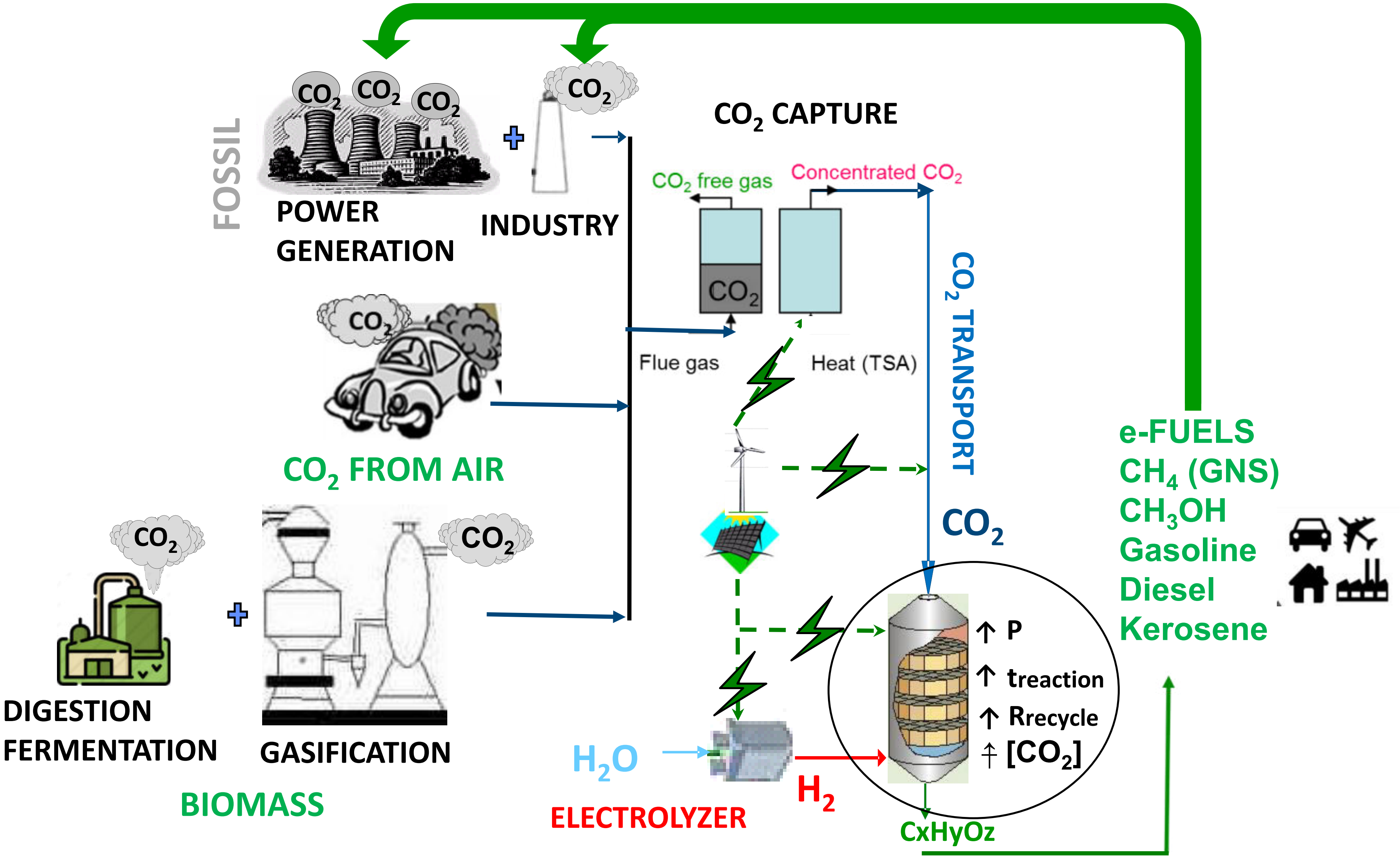
Advantages of e-fuels

- ↑ Reduction of CO_2 emissions vs. conventional fossil fuels
- ↑ Ease of storage vs. electricity & H_2
- ↑ Energy density vs. electricity & H_2 ⇒ Usable in sectors of difficult electrification (aviation, maritime, heavy transport)
- Infrastructures for storage, transport and use (energy generation or mobility) fully developed.

Power-to-Fuels (e-fuels) deployment bottlenecks

- ↓ Energy efficiency in fuel production (losses associated with conversion steps)
- ↓ Level of development (Demo) of the technology (few commercial plants or in↑ TRLs)
- ↑ CAPEX (electrolyzers)
- ↑ Production costs vs. conventional fossil fuels

Power-to-Fuels: CO_2 capture and conversion



CO_2 CO_2 CO_2 CO_2

FOSSIL

POWER GENERATION + INDUSTRY

CO_2

CO₂ FROM AIR

CO_2 CO_2

DIGESTION FERMENTATION + GASIFICATION

BIOMASS

CO_2 CAPTURE

CO_2 free gas

Concentrated CO_2

CO_2

Flue gas

Heat (TSA)

CO_2 TRANSPORT

CO_2

H_2O

ELECTROLYZER

H_2

↑ P

↑ treaction

↑ Rrecycle

↑ $[CO_2]$

CxHyOz

e-FUELS

CH_4 (GNS)

CH_3OH

Gasoline

Diesel

Kerosene

$$(2x-z+y)\ H_2 + x\ CO_2 \leftrightarrow (2x-z)\ \ H_2O + C_xH_yO_z$$

CO$_2$ capture and hydrogenation: Process Intensification

Challengues: Increase energy efficiency (ηe) and decrease CAPEX & OPEX

⇩

- ↑ Efficiency, selectivity & tolerance poisons →↓P & T⇒↑ηe
  →↓$V_{reactor}$⇒↓CAPEX
- ↑ Lifetime ⇒ ↓ Deactivation (C, H_2O+ ↑ T) or regeneration ⇒ ↓OPEX
- Reactor design optimization: T control/heat integration ⇒↓CAPEX & ↑ηe

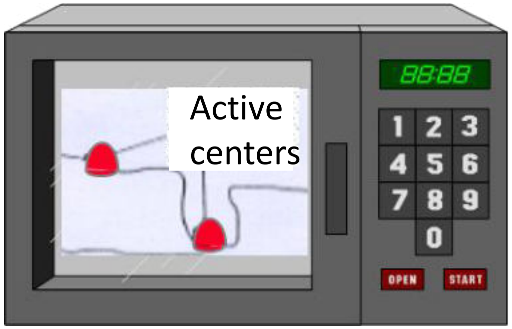
⇩

Process intensification: Combination of CO$_2$ capture and/or catalytic hydrogenation of CO$_2$ with other processes or operations in a single, more efficient and compact reaction system:

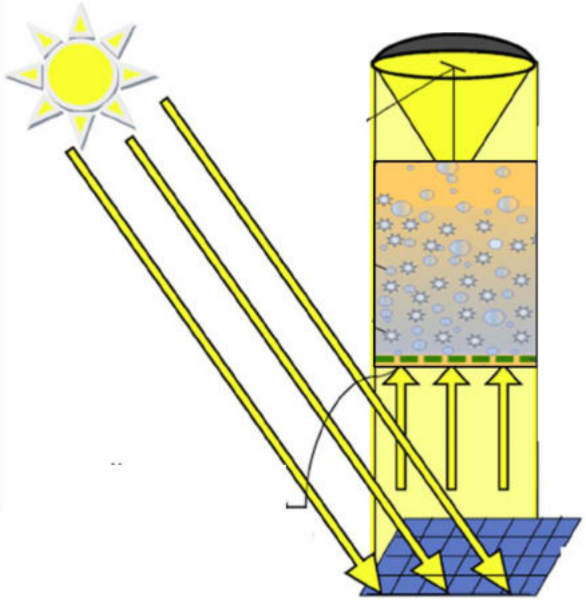
- Alternative reaction heating (microwave, solar)
- Selective activation (photoelectro/photo/electro-catalysis, plasma)
- Reactor design (reaction-heat exchange, reaction-separation)
- Cyclic operation (reaction/adsorption-desorption)

Alternative ways of reaction heating

T active centers > T bulk catalyst

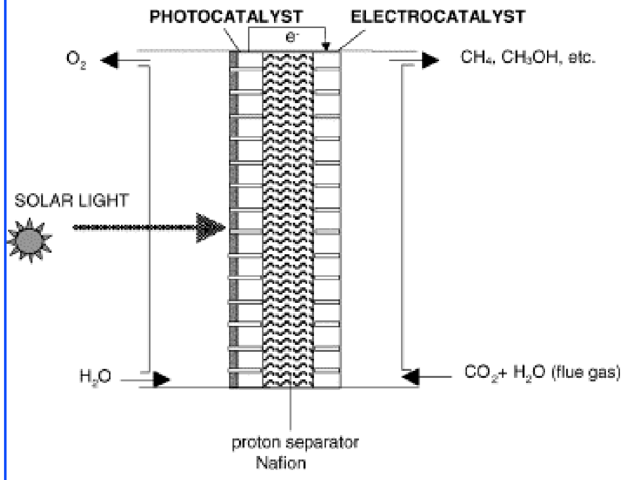


Microwave energy



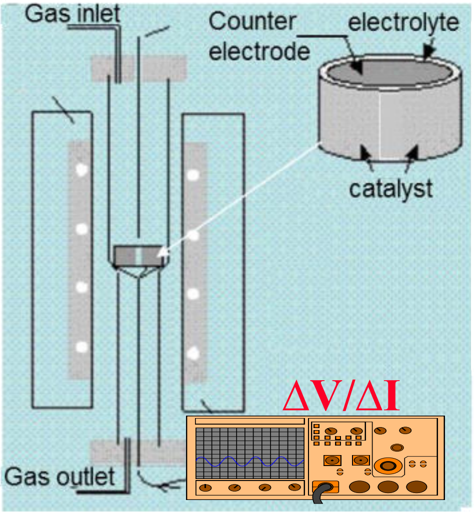
Concentrated solar thermal

Selective activation

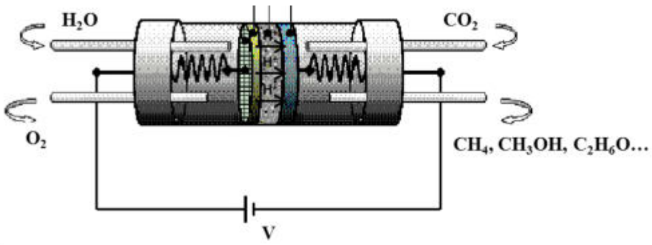


Photoelectrocatalysis

Single chamber SOEC



Double chamber SOEC

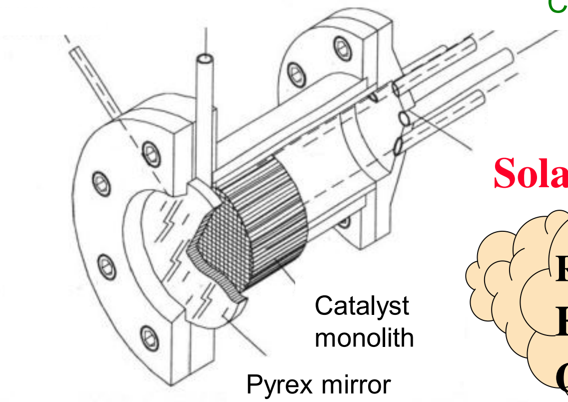


Source: C.G. Vayenas et Al., Electrochemical Activation of Catalysis: Promotion Electrochemical Promotion and Metal-Support Interactions, 2001

Electrocatalysis in Solid Oxide Electrolyte Cells (SOEC)

$CO_2 + H_2$

DME, CH_4, CH_3OH



Photocatalysis

Solar light

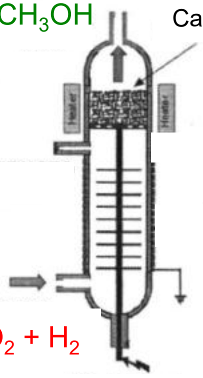
Electric discharge

Reactive species

H^* O^*

OH^* CO_2^*

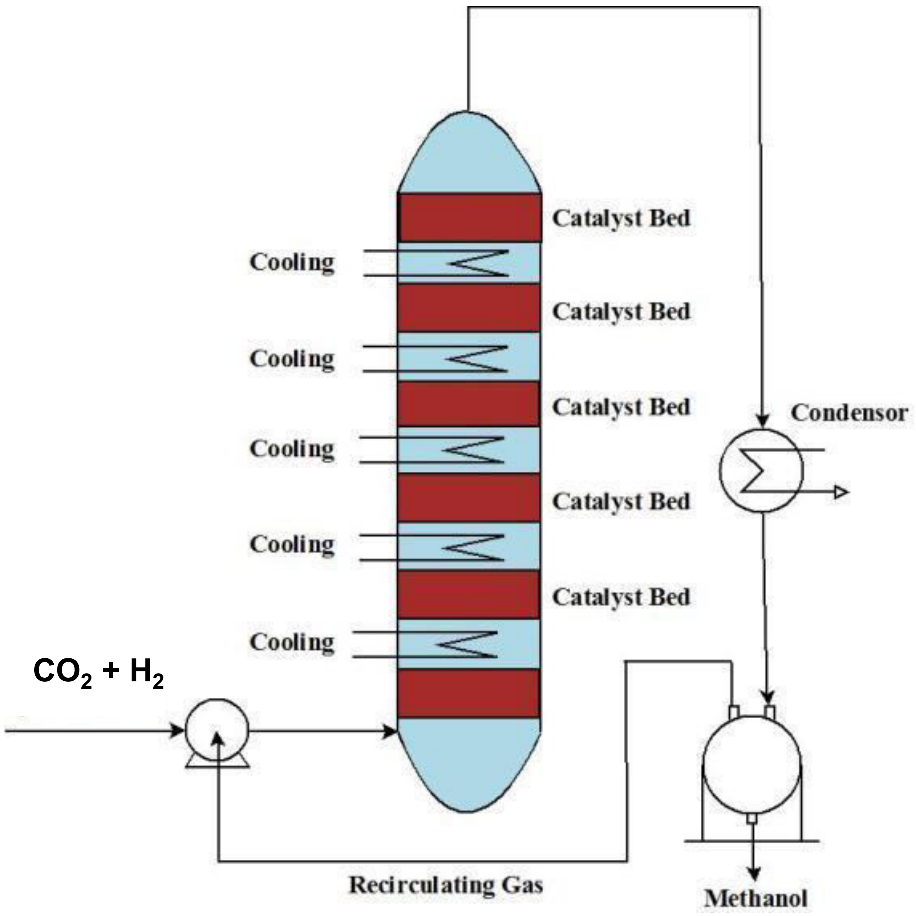
DME, CH_4, CH_3OH



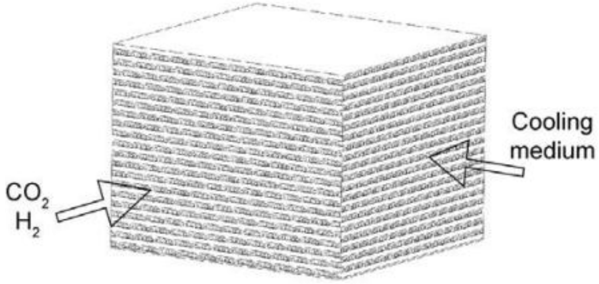
$CO_2 + H_2$

Plasma asissted Catalysis

Reactor design optimization: Heat integration

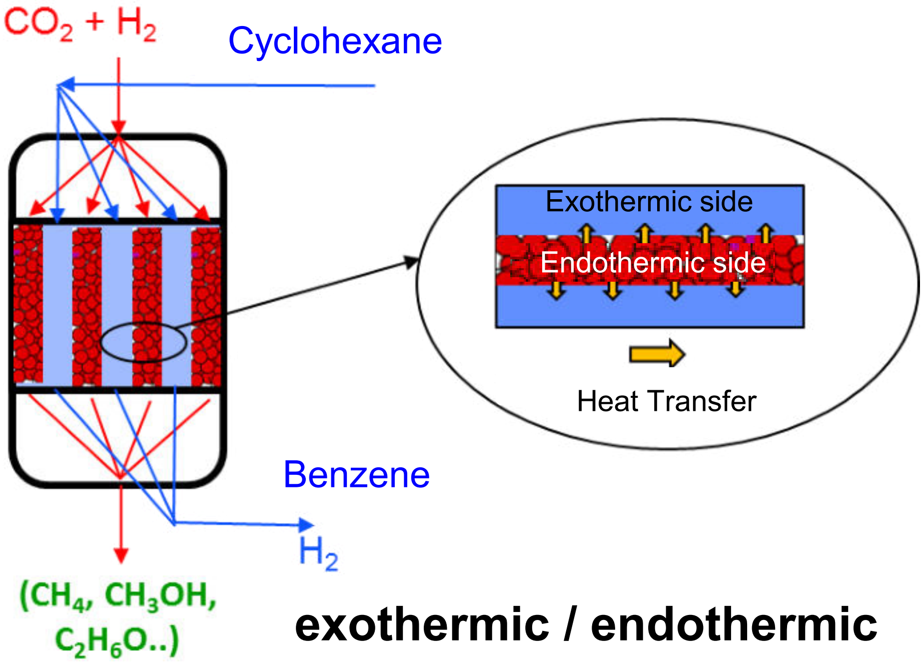


Recirculation/ intercooling



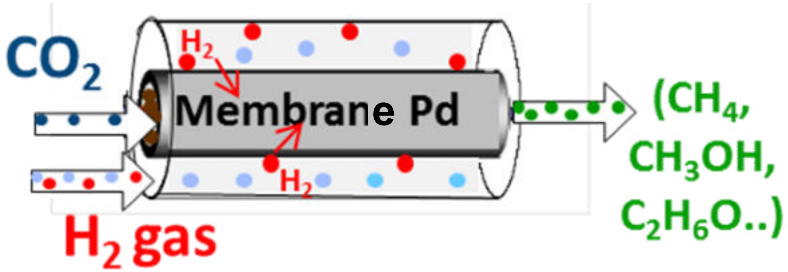
Source: K. Ghaib et Al., Renewable and Sustainable Energy reviews 81 2018 433-446

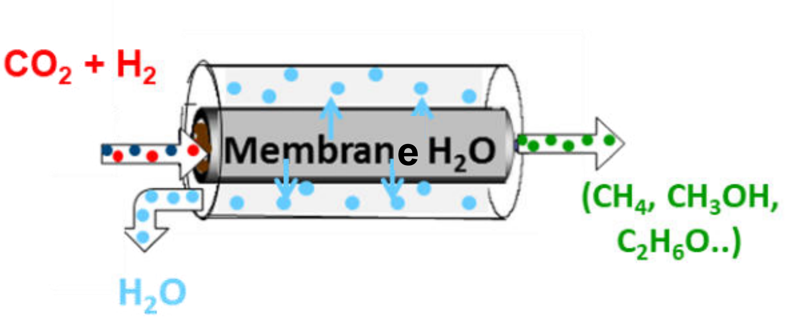
Microchannels

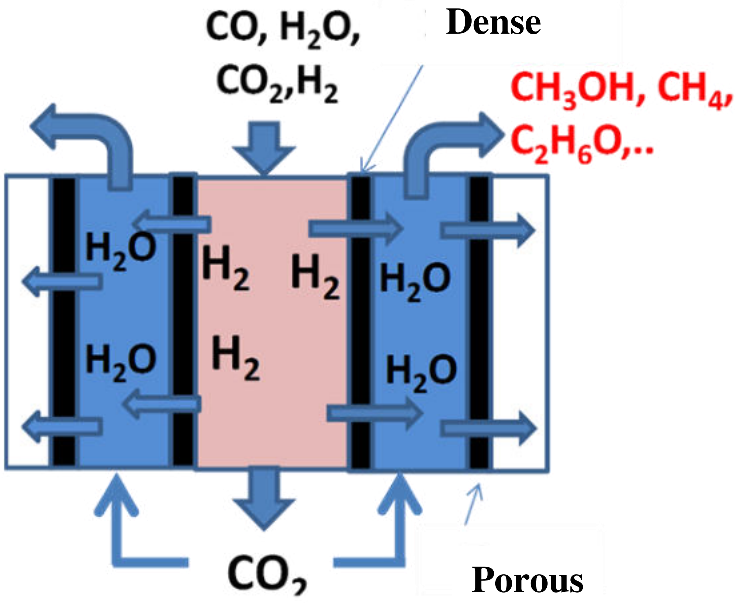


exothermic / endothermic

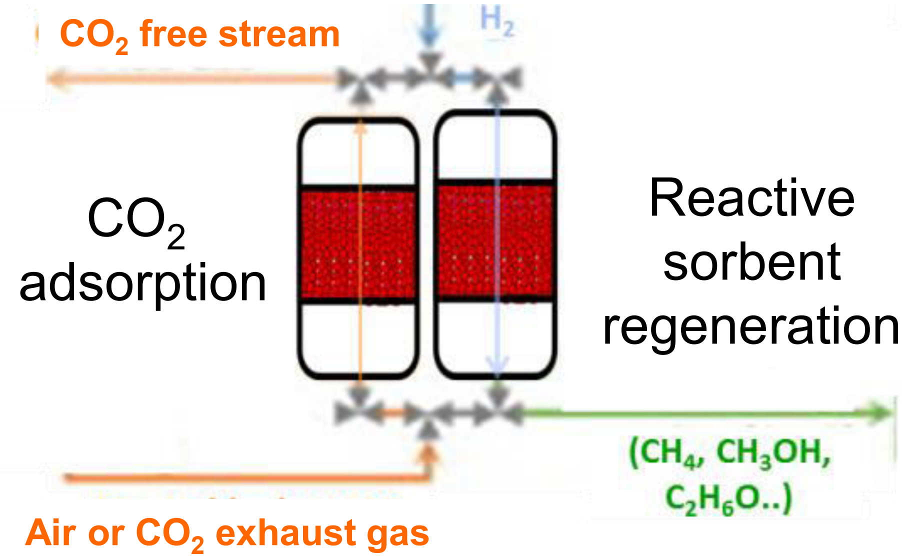
Reactor design optimization: in-situ separation







Cyclic operation (reaction-adsorption)



CO_2 free stream

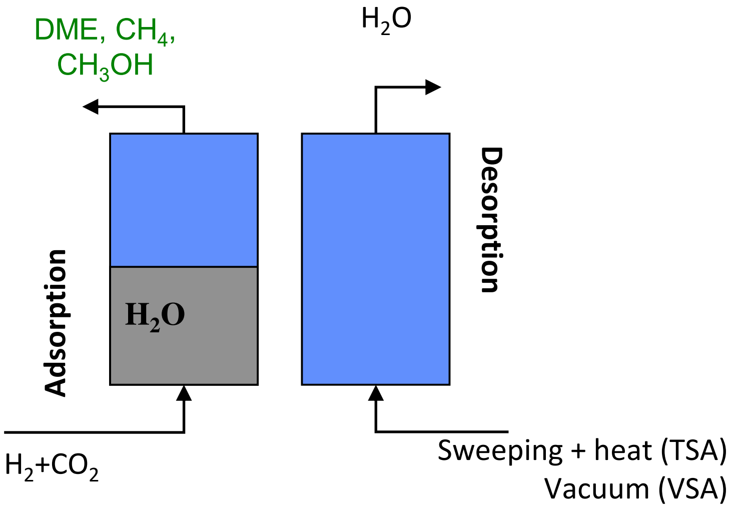
H_2

CO_2 adsorption

Reactive sorbent regeneration

(CH_4, CH_3OH, C_2H_6O..)

Air or CO_2 exhaust gas



DME, CH_4, CH_3OH

H_2O

Adsorption

H_2O

Desorption

H_2+CO_2

Sweeping + heat (TSA)
Vacuum (VSA)

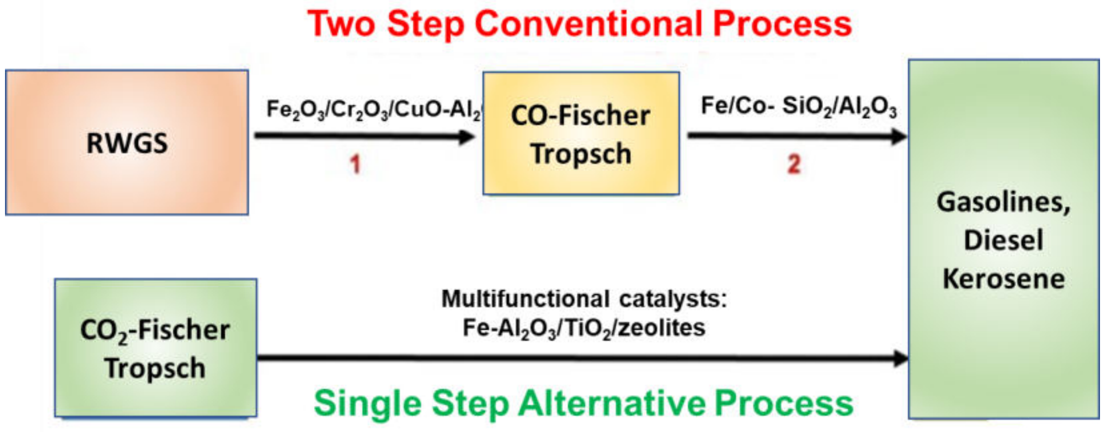
Multifunctional catalysts

Multicatalytic materials combining active phases for different step reactions (e.g. RWGS/CO-Fischer Tropsch/hydroisomerization)

Indirect Fischer-Tropsch synthesis: RWGS + CO-FT (TRL 9 – commercial)

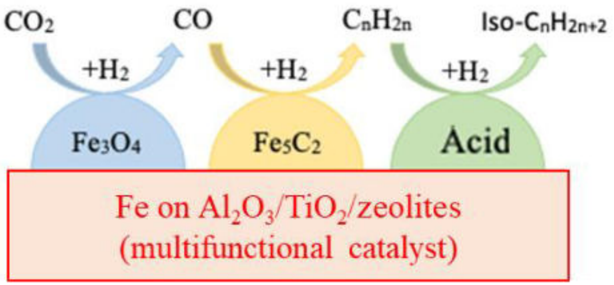
$H_2 + CO_2 \rightarrow CO + H_2O$ (Reverse Water Gas sifth- RWGS)

$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$ (Fischer Trospch- FT)



Direct Fischer-Tropsch Synthesis: CO_2-FT (TRL 3-5)

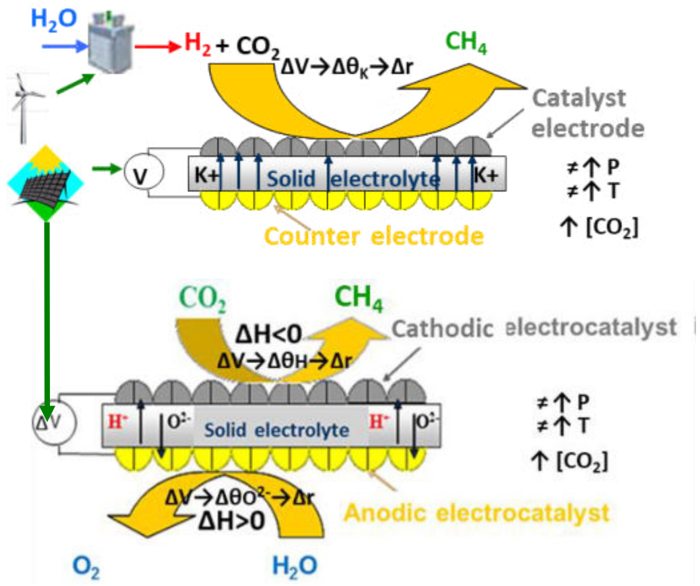
$n\ CO_2 + (4n+1)\ H_2 \rightarrow C_nH_{n+2} + 2n\ H_2O$



Source: Wei and col., ACS Catal 2018: 8, 9958–9967, Liu and col., Catalysts 2019: 9, 275

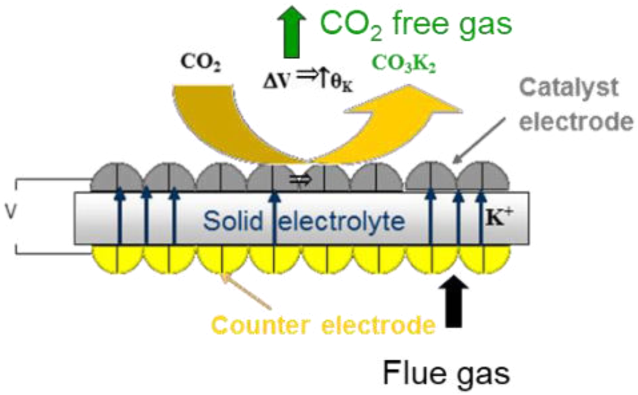
CIEMAT Research: Electrochemical selective activation

- Selective catalyst activation by combination of CO_2 hydrogenation at atmospheric pressure with electrochemical promotion of the catalyst in single-chamber SOEC to enhance activity and selectivity.
- Selective catalyst activation by combining CO_2 hydrogenation at atmospheric pressure with H_2O electrolysis for in-situ production of H_2 in double chamber SOEC (Co-electrolysis)

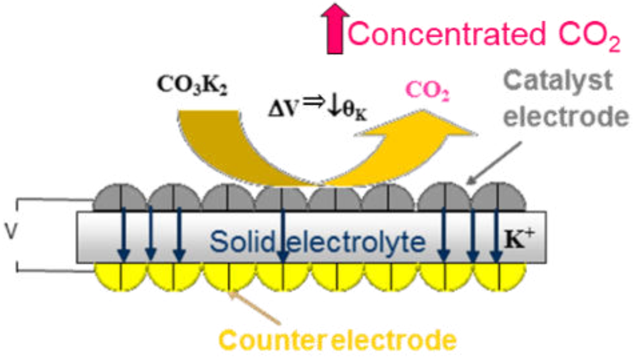


- Electropromoted CO_2 capture by selective activation of adsorbent, using a small ΔV (ESA) instead of more energy intensive ΔT/ΔP (TSA/PSA) in single chamber SOECs

ADSORPTION



DESORPTION



CIEMAT Research: Electrochemical selective activation

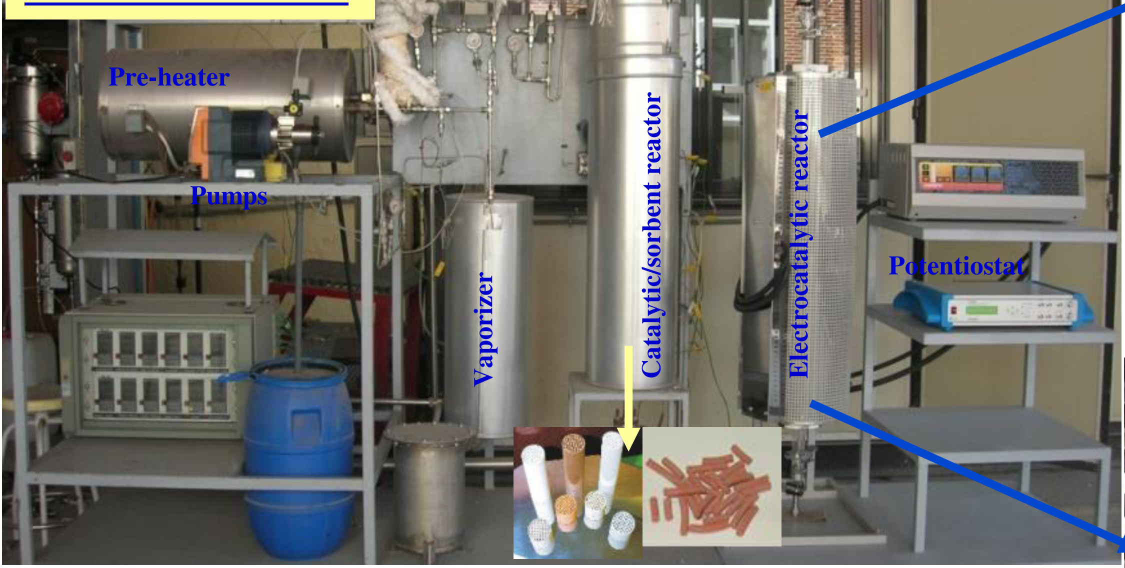
- Flow rate: up to 20 Nm^3/h
- Temperature: up to 900 º C
- Pressure: atmospheric

Gas Supplying Unit: CO_2, H_2, Air, SO_2, NO, CO, CH_4, N_2…

Blending Unit

PILOT PLANT

Catalytic/sorbent/Electrocatalytic



Single chamber reactor

Double chamber reactor

GAS ANALYSIS SYSTEM

NDIR CO_2/CO

GC-FID

Micro-GC

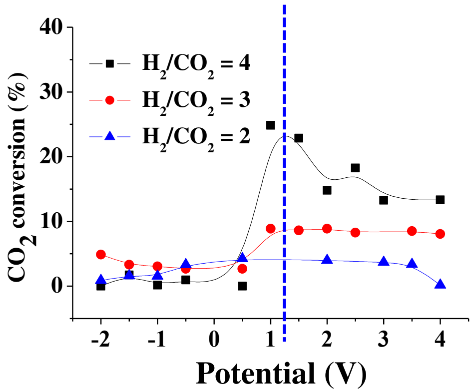
TCD-H_2

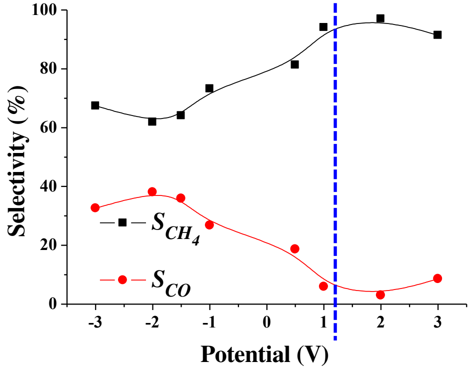
GC-MS

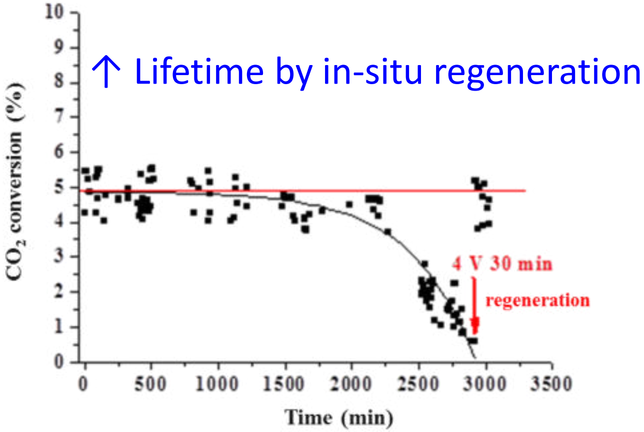
Electrochemically enhanced CO_2 hydrogenation

- ✓ Maximize CH_4 yield: CO_2 conversion (XCO_2) & selectivity (S_{CH4}) & in-situ regeneration
- ✓ Minimize energy input: maximize faradaic efficiency (η_c) & minimize energy cost (C_E)

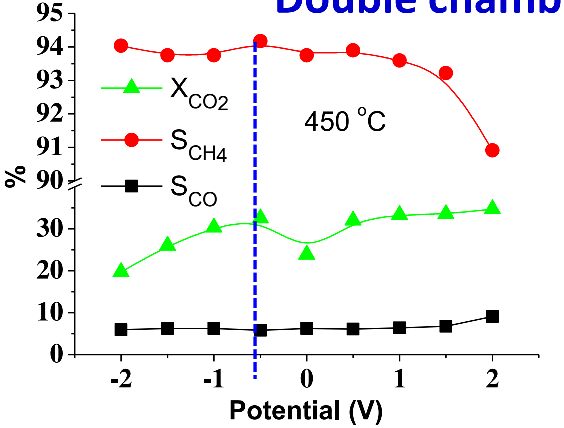
Single chamber reactor (electrochemical promotion)

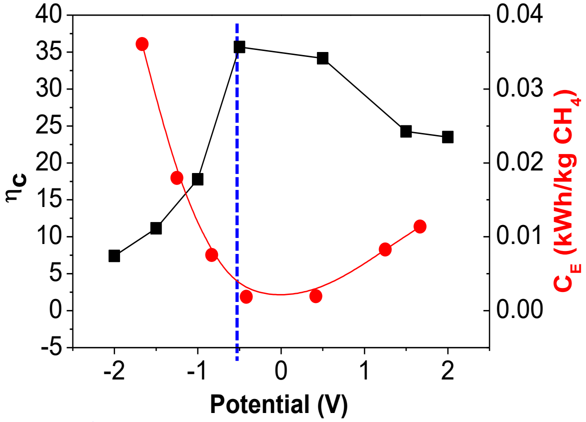





↑ Lifetime by in-situ regeneration

Double chamber reactor (co-electrolysis)

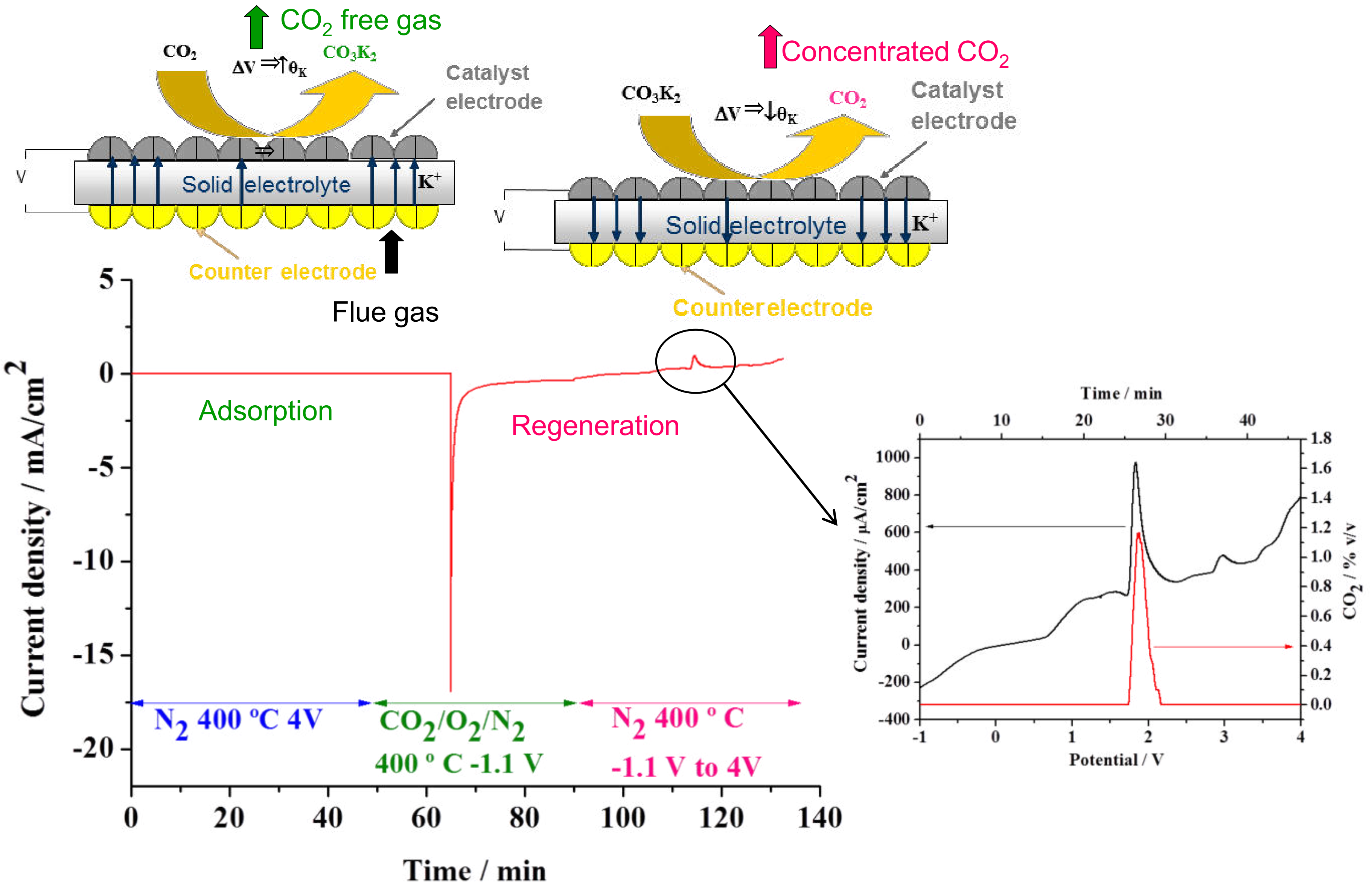




↓ *CH_4 purification cost:*
↑XCO_2. ↑ Sel_{CH4} ↓*Sel_{CO}*

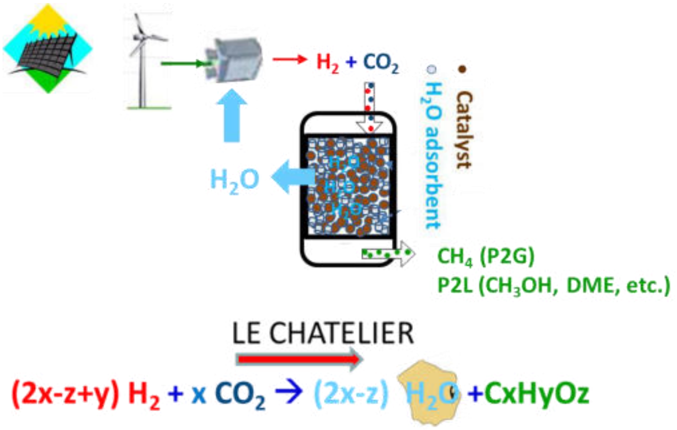
↑ Energy Efficiency:
η_c Max. & C_E Min.

Electrochemically mediated CO_2 capture

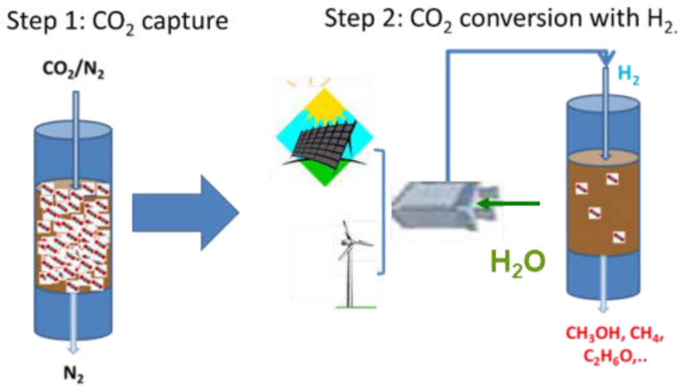


CIEMAT Research: Cyclic operation (reaction-adsorption)

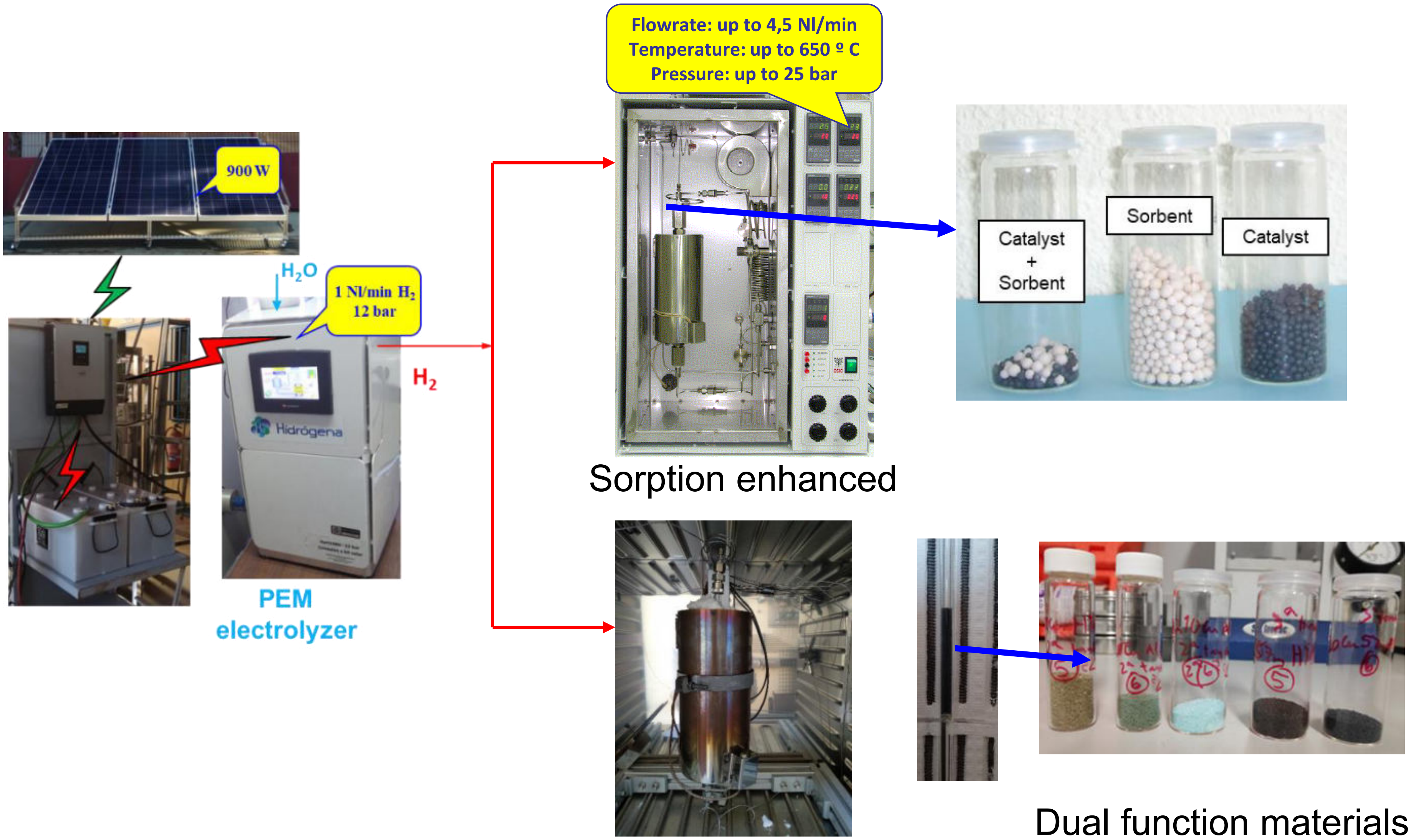
- Sorption enhanced catalytic CO_2 hydrogenation, by combining an active catalyst and a water selective adsorbent, to shift the equilibrium conversion via in situ water removal.



- CO_2 capture and hydrogenation by reactive adsorption, using dual function materials (CO_2 sorbent & hydrogenation catalyst) by coupling endothermic CO_2 desorption step with exothermic CO_2 hydrogenation step in a single isothermal reactor at atmospheric pressure



CIEMAT Research: Cyclic operation (reaction-adsorption)



Flowrate: up to 4,5 Nl/min
Temperature: up to 650 º C
Pressure: up to 25 bar

PEM electrolyzer

Sorption enhanced

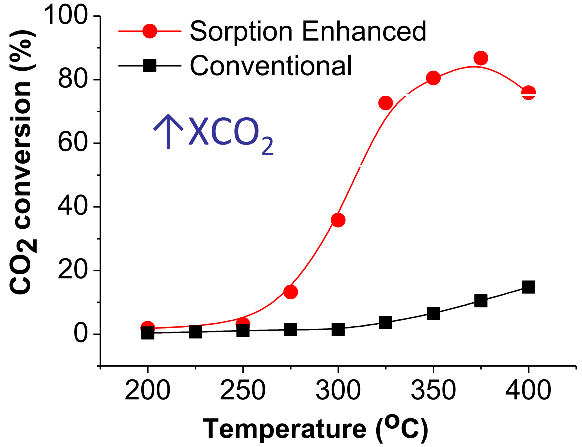
Dual function materials

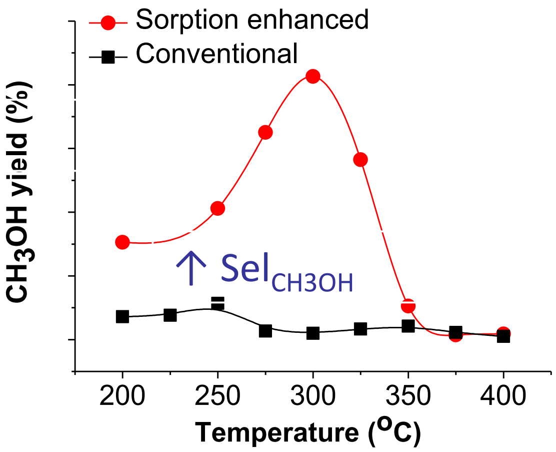
Reactive adsorption

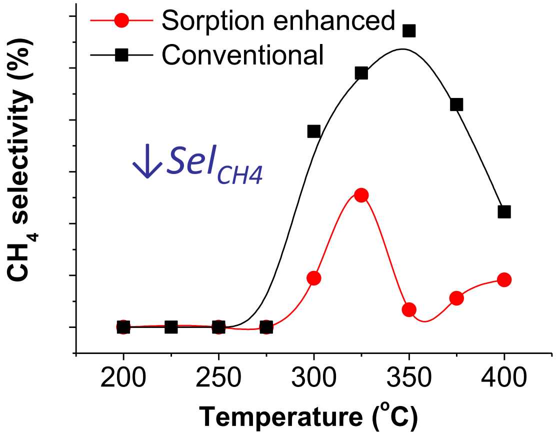
CIEMAT Research: Cyclic operation (reaction-adsorption)

- ✓ Maximize CH_3OH/CH_4 yield: CO_2 conversion (XCO_2) & selectivity (S_{CH4})
- ✓ Minimize energy input: Heat integration ΔQreaction (exothermal)↔ΔQregeneration (endothermal)

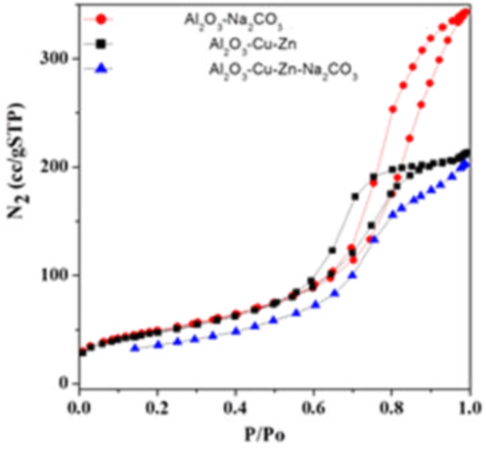
Sorption enhanced catalytic CO_2 hydrogenation



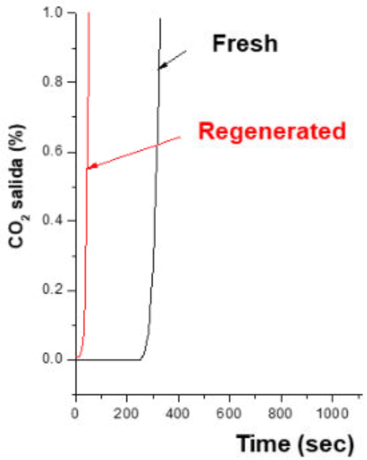




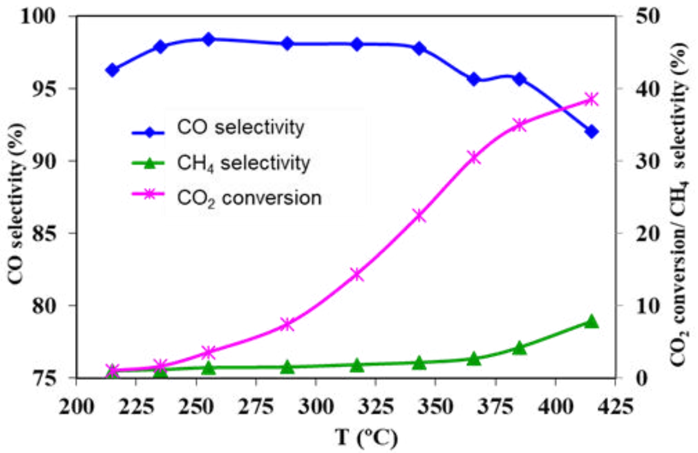
Reactive-adsorption for in-situ CO_2 capture and hydrogenation



BET curves comparison



CO_2 capture on Al_2O_3-Na_2CO_3



CO_2 methanation on Al_2O_3-Cu-Zn-Na_2CO_3

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DE ESPAÑA

MINISTERIO
DE CIENCIA
E INNOVACIÓN

Ciemat
Centro de Investigaciones
Energéticas, Medioambientales
y Tecnológicas

Esperanza Ruiz Martínez
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Thank you for your attention!

High temperature electrolysis and co-electrolysis for production of green hydrogen and syngas

Ville Saarinen

VTT fuel cells and hydrogen

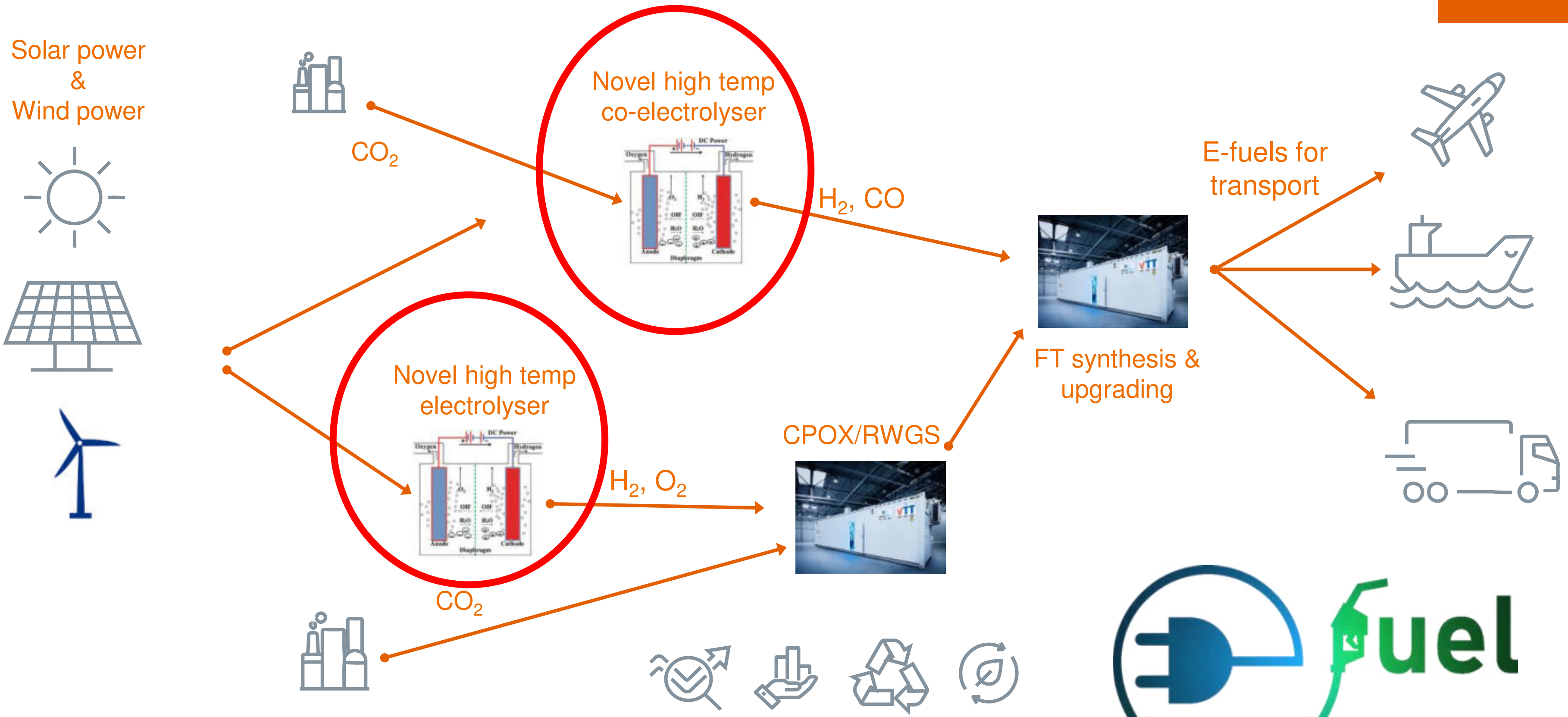
11.2.2022

VTT – beyond the obvious

VTT Fuel cells & Hydrogen

- 20 years of active history in PEMFC, SOFC, and electrolysis
- ~50 person involved in H_2 related activities at VTT
- Mainly working with European and Finnish companies in EU-projects and contract research, currently coordinating 7 EU-projects and participating in 17 projects
- All activities are supported by validated modeling tools (CFD, thermal, mechanical, etc.) from single components to complete systems
- Excellent know-how, research facilities, wide international partner network and long experience on high temperature electrolysis and fuel cells
- Product development for Industrial partners: sales and licensing IPR for Finnish and European companies
- https://www.vttresearch.com/en/ourservices/fuel-cells-and-hydrogen

rSOC and E-fuel Concept to be demonstrated



Solar power
&
Wind power

CO_2

Novel high temp
co-electrolyser

H_2, CO

Novel high temp
electrolyser

H_2, O_2

CO_2

CPOX/RWGS

FT synthesis &
upgrading

E-fuels for
transport

System analysis, TEA, LCA, fuel markets & business development

Motivations to develop electrolyser technology

- According to Hydrogen Europe, an additional **20-40 GW** of renewable generation can be accommodated by 2030 as a result of hydrogen production by electrolysis (i.e. power-to-gas), resulting in the transfer of **70-140 TWh** of Europe's renewable energy to other sectors.
- Efficiency improvements in production process (OPEX) in the coming future can be estimated maximum in around 10%. Electricity is the main cost component affecting the price of hydrogen.
- **<u>The size of water electrolyser market measure in power is around 100 MW. This will grow into 1000 – 10 000 fold in coming years.</u>** It is inevitable that remarkable reductions in production costs of equipment (CAPEX) will be achieved.

Electrolyser Technologies

	ALKALINE	PROTON EXCHANGE MEMBRANE (PEM)	SOLID OXIDE (SOE)
☺	Low capital cost Mature technology	Fast start-up Commercial technology Smaller footprint	High electrical efficiency Co-electrolysis (H_2O & CO_2) Reversible operation
☹	Limited operation flexibility High operational cost	High capital cost, if high efficiency targeted	R&D pre-commercialized
System scale	Up to 100 MW	Up to tens of MW	Up to 1 MW
System cost excl.	Public: 1000-1200 €/kW* 2018 offers: 700 €/kW**	1900-2300 €/kW* 2018 offers: 800-900 €/kW**	*target <2000 €/kW by 2020 (now: 4000 €/kW, mass production 1500 €/kW)*
Electrical efficiency	75% (HHV), 63 % (LHV)**	68% (HHV), 58 % (LHV)**	80-90%

*Development of water electrolysis in the EU, 2014:
** 20 MW size (2018 offers).
Capital cost depends on efficiency

Incl. power supply, system control, gas drying (purity above 99.4%). Excl. grid connection, external compression, external purification and hydrogen storage, building

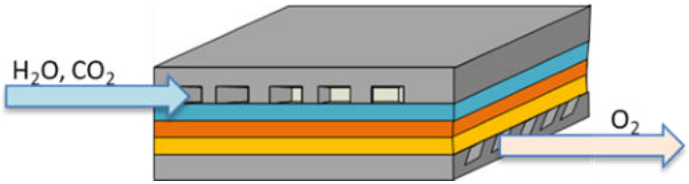
Solid oxide electrolyser (SOEC) operation principle

- Steam electrolysis

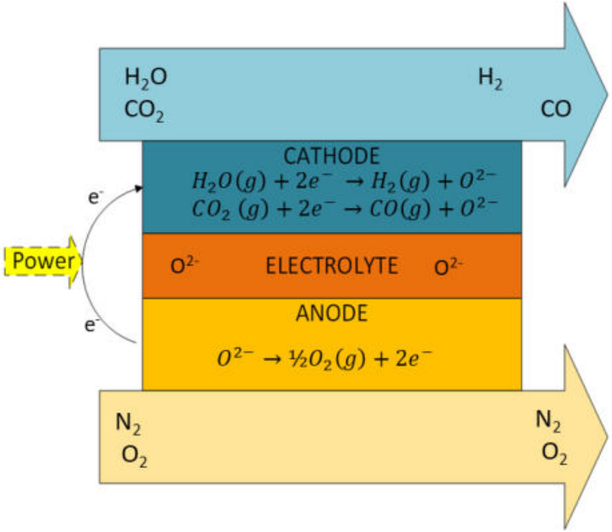
$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad \Delta H \approx 250\ \text{kJ/mol}$$

- Co-electrolysis

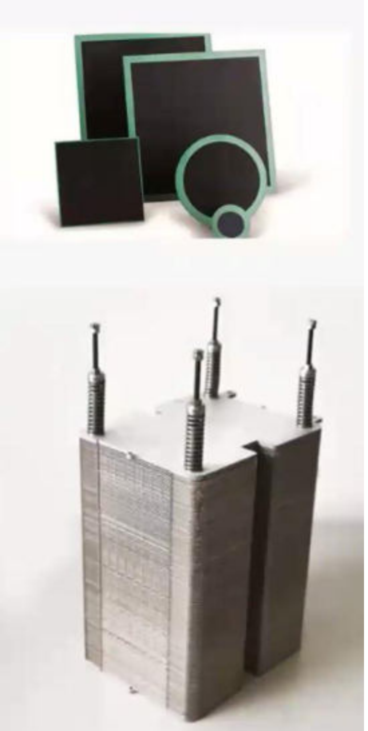
$$H_2O + CO_2 \rightarrow H_2 + CO + O_2 \qquad \Delta H \approx 525\ \text{kJ/mol}$$



Simplified figure of SOEC cell structure

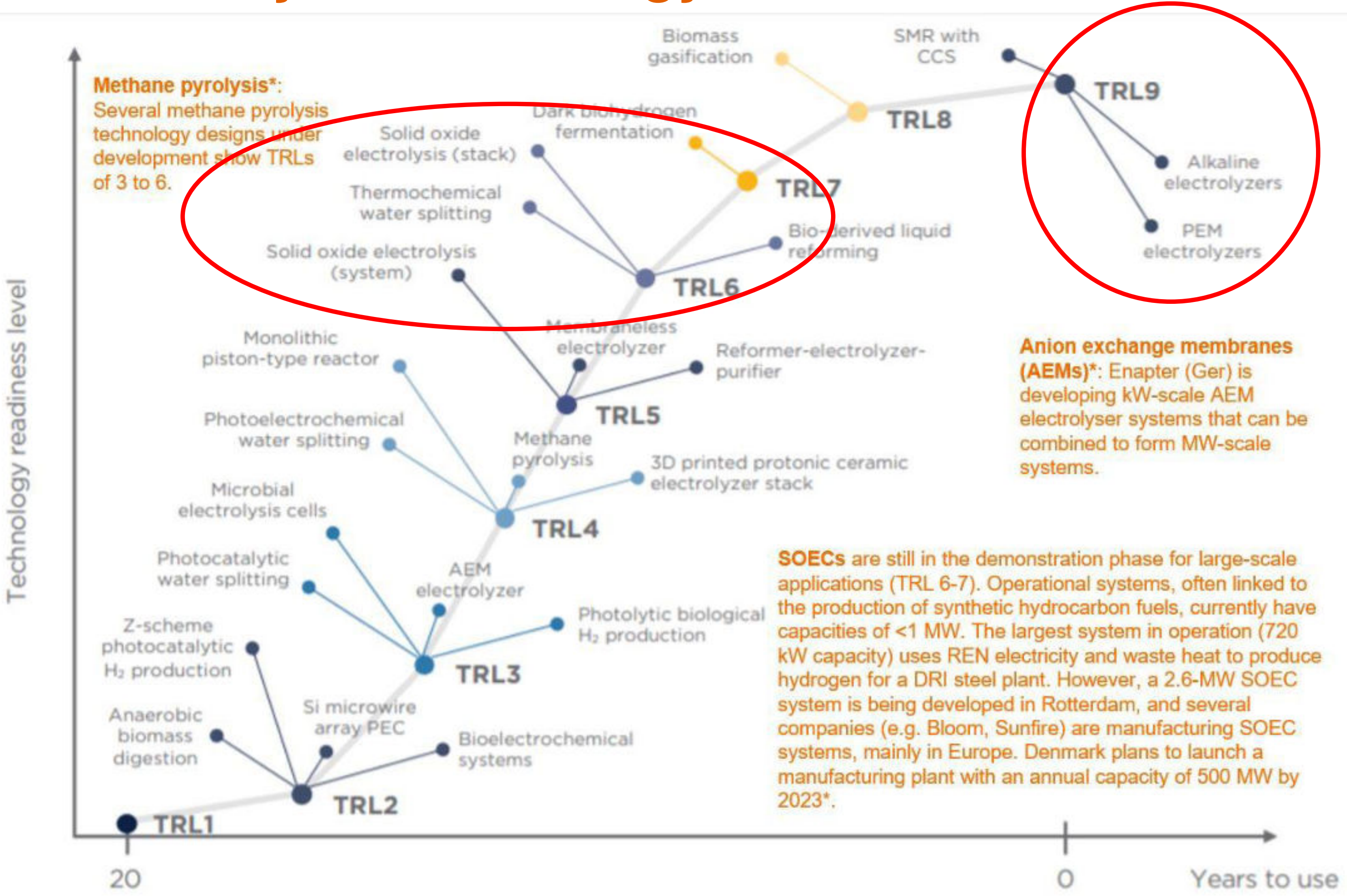


Solid oxide technology



- High operation temperature: 600-850 ^{o}C
- **SOE technology offer the potential for highest electrical efficiency in electrolysis mode (80-90%) compared to other electrolyser technologies**
- **SOEC technology is reversible**: the same system can work both as a fuel cell and an electrolyser depending on power generation and grid stabilisation needs
- **SOEC has capability also for co-electrolysis of steam and CO_2, which enables more efficient power-to-X, if integrating SOEC as part of industrial processes**
- The most commercial electrolysers are nowadays alkaline, but process has low efficiency due to needed high operation voltage. PEM based technology is more expensive than alkaline and it has also its own limiting factors like availability of iridium catalyst

Electrolyser technology readiness



Methane pyrolysis*: Several methane pyrolysis technology designs under development show TRLs of 3 to 6.

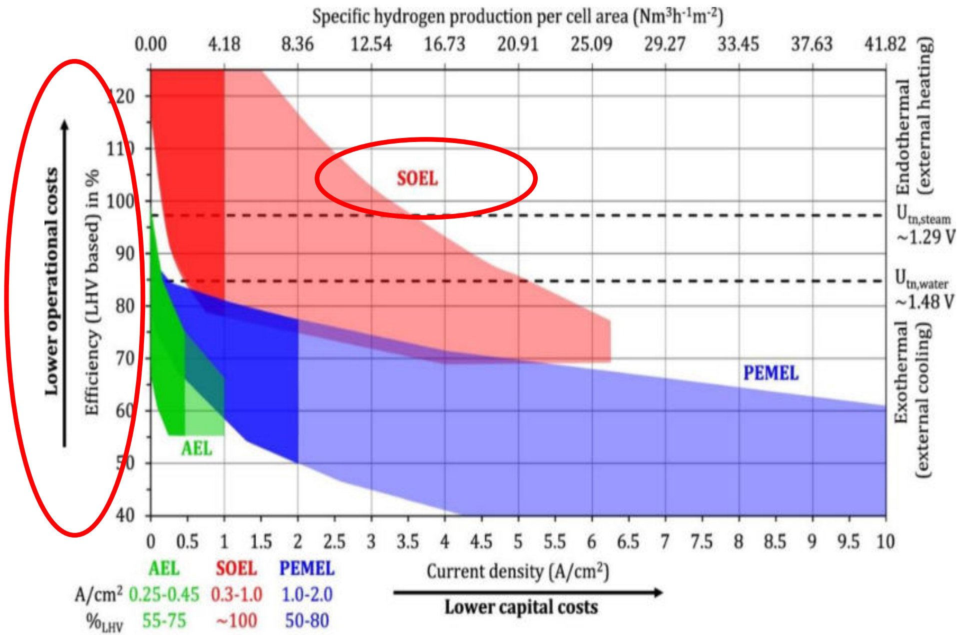
Anion exchange membranes (AEMs)*: Enapter (Ger) is developing kW-scale AEM electrolyser systems that can be combined to form MW-scale systems.

SOECs are still in the demonstration phase for large-scale applications (TRL 6-7). Operational systems, often linked to the production of synthetic hydrocarbon fuels, currently have capacities of <1 MW. The largest system in operation (720 kW capacity) uses REN electricity and waste heat to produce hydrogen for a DRI steel plant. However, a 2.6-MW SOEC system is being developed in Rotterdam, and several companies (e.g. Bloom, Sunfire) are manufacturing SOEC systems, mainly in Europe. Denmark plans to launch a manufacturing plant with an annual capacity of 500 MW by 2023*.

Source: Columbia SIPA (Aug 2021): Green hydrogen in a circular carbon economy: Opportunities and limits ; IEA (Oct 2021)*: Global Hydrogen Review 2021

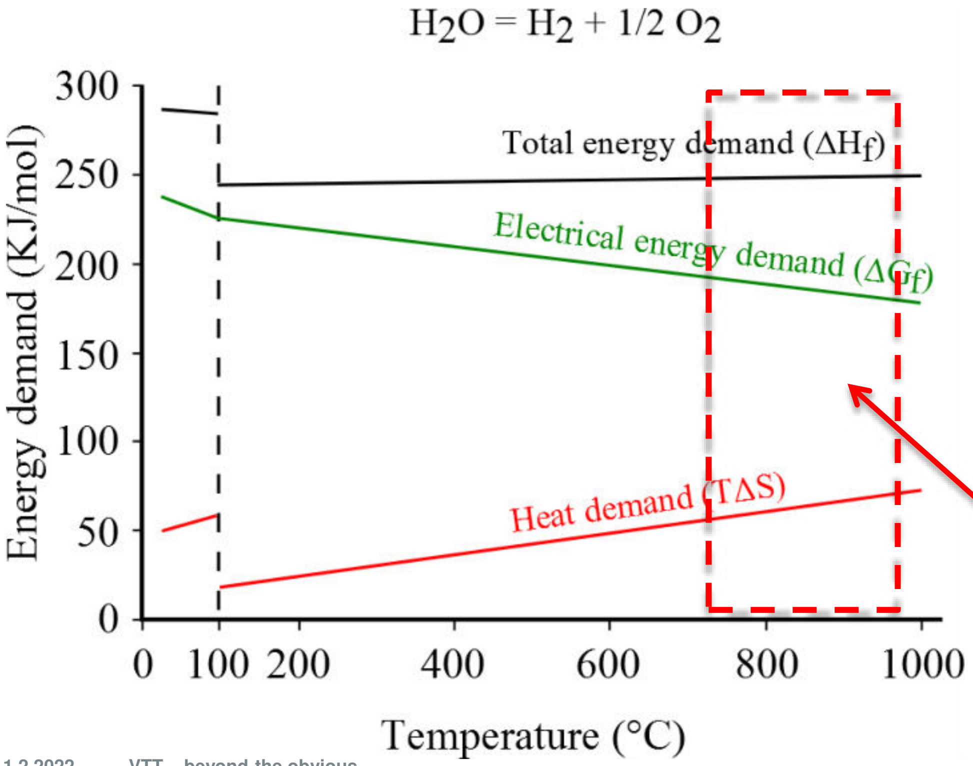
Efficiency can be improved without tradeoff

- Efficiency can be increased by
  - electrolyte and separator development (thinner, higher conductivity, better durability)
  - catalyst development (higher activity, better durability)
  - Reactant and product transport improvement (flow field, transport layer)
- Continuous field of development
- No theoretical limitation on efficiency (except energy balance)



Summary of efficiency and operational range of AE, PEME and SOE cells or stacks. (Buttler & Spliethoff, 2018).

Benefit of high temperature electrolysis originates from thermodynamics



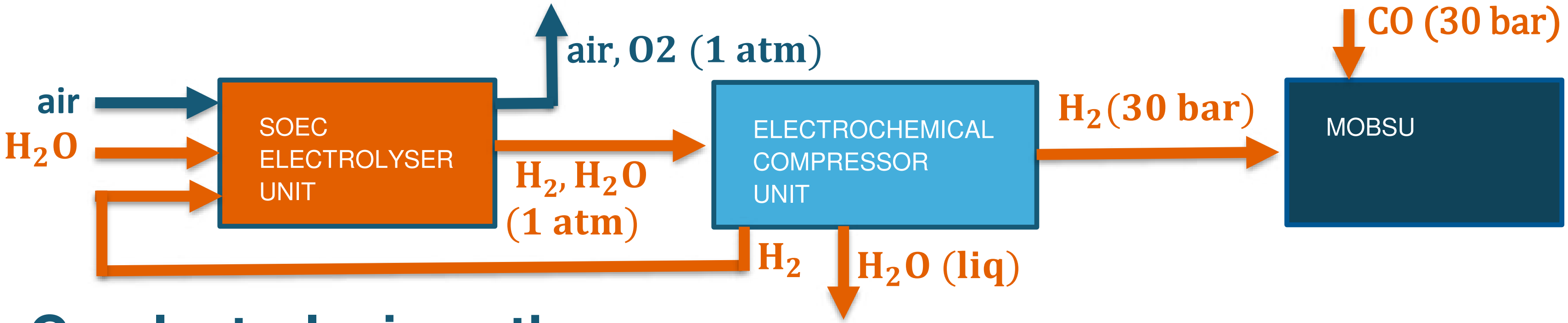
- **Lower activation losses** at lower current densities at high temperatures (700-800 °C) lead to **lower power consumption** during hydrogen production
- **No need for noble metal catalysts**
- **Solid oxide cells and stacks can be made with low cost raw materials** (suitable for mass manufacturing)

High temperature electrolyser operation

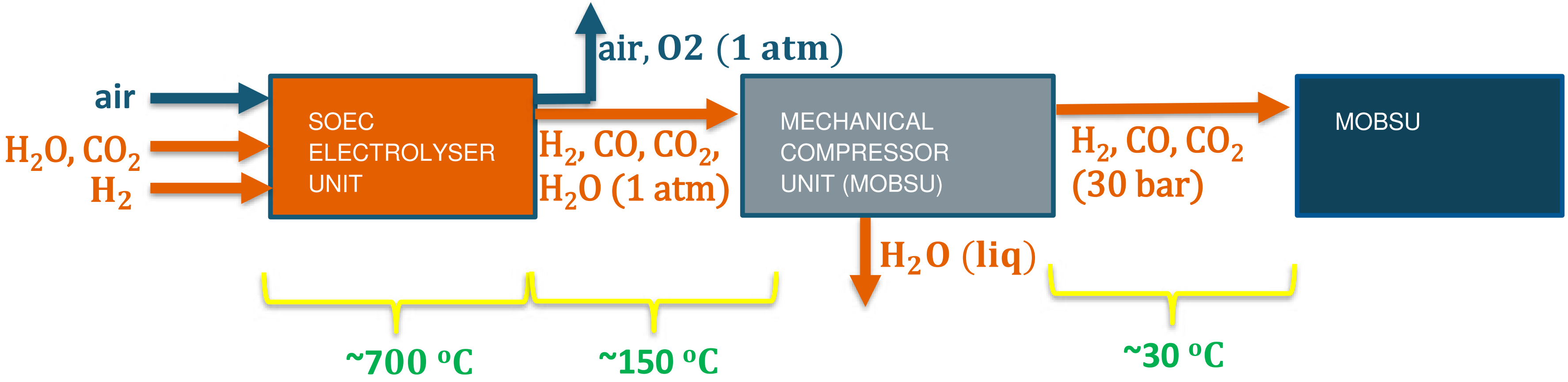
Co-electrolysis of CO_2 and steam

- Solid Oxide electrolysis can perform CO_2 and steam co-electrolysis and produce syngas ($CO + H_2$)
- The technology is essentially the same as for pure hydrogen production
- Thermal integration between electrolysis and downstream synthesis steps highly beneficial
- Benefits of co-electrolysis compared to electrolyser and reverse water gas shift reactor:
  - Simpler layout
  - rWGS needs high temperature (>>600°C), difficult to couple with low-temperature electrolyser
- Drawbacks:
  - CO_2 need to be highly pure for co-electrolysis
  - Risk of carbon deposition

Electrolysis pathway:

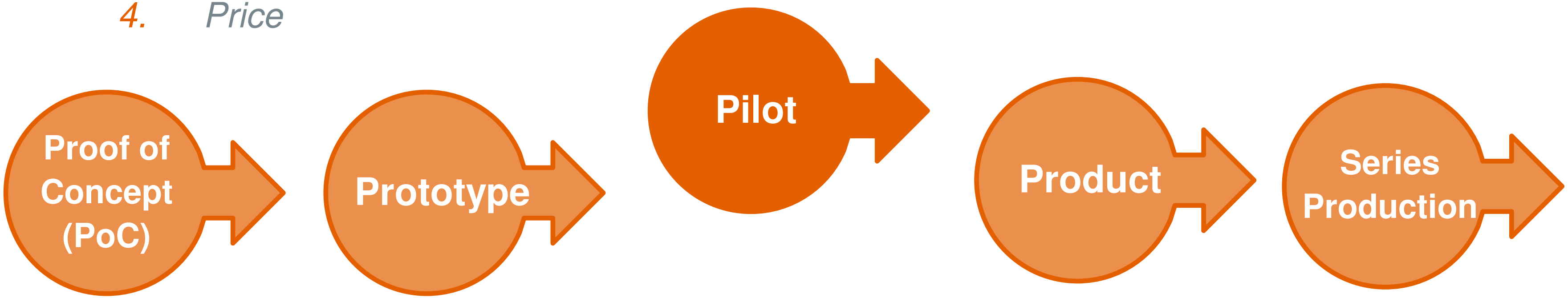


Co-electrolysis pathway:



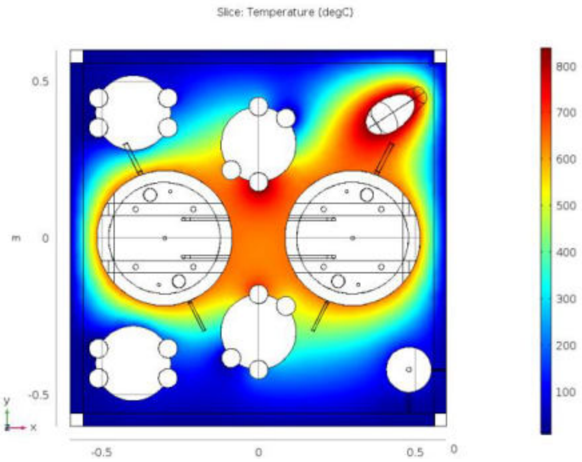
Designing aspects for reversible solid oxide pilot system

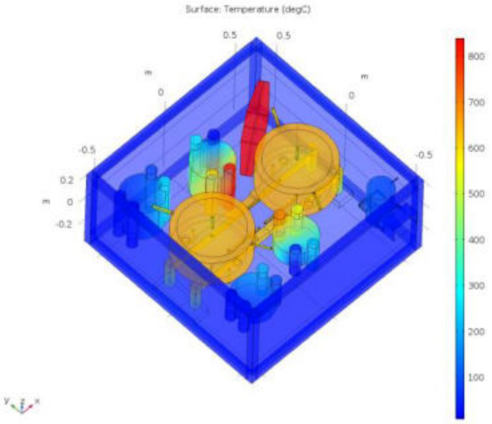
- Developing, testing and learning about new technology
- Modelling and finding system boundaries for optimized system
- End users main points of interest for a rSOC system:
  1. *Efficiency*
  2. *Operation window*
  3. *Lifetime of the system*
  4. *Price*



rSOC pilot system «RESSU»

- Highly instrumented **Re**versible **S**OC **S**ystem **U**nit “**RESSU**” designed and build by VTT
- High efficiency and suitable for integration with various energy sources and P2X, adaptability to local energy needs (supports grid stabilisation with high penetration of renewable electricity)
- Good technology base for green, flexible and efficient energy systems





Measured system level efficiency

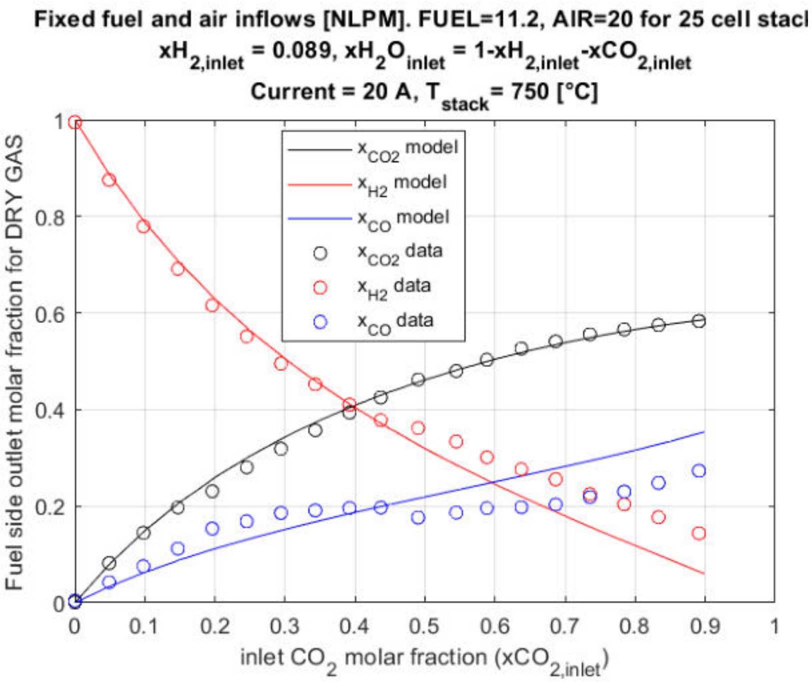
$$\eta_{AC\ to\ H_2}(HHV\ or\ LHV) = \frac{HHV\ or\ LHV\ of\ produced\ H_2}{Total\ AC\ power\ input}$$

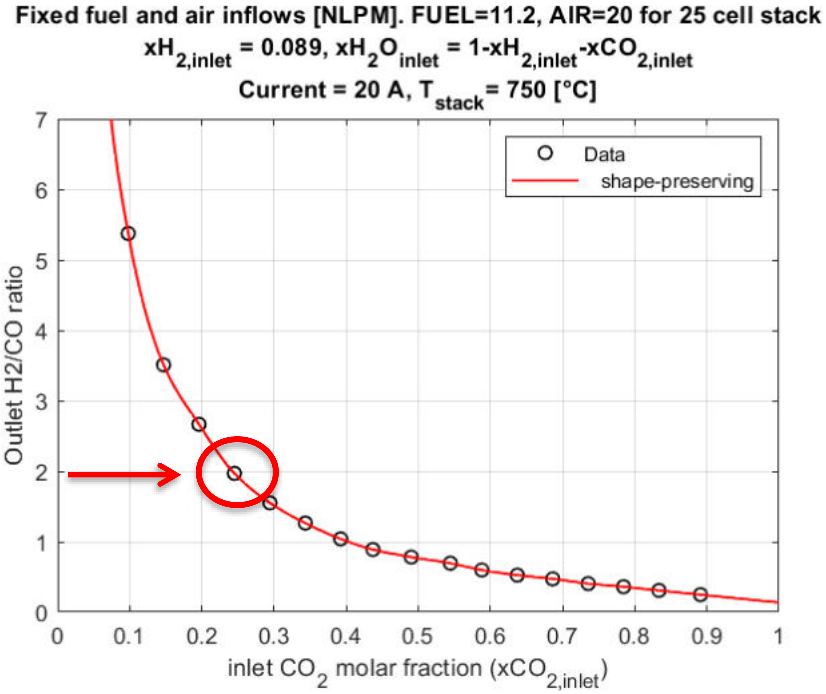
- where *Total AC power input = AC power input for electrolysis + AC power input for heaters + AC power input for evaporator*
- The *AC power input for electrolysis* includes all AC power consumed by the power supply. This term also takes into account the voltage losses outside the stack, the power consumption of the power source, and the AC/DC conversion efficiency

rSOC system level	AC power for steam production included	Free 150 ^oC steam flow assumed
AC to H_2 efficiency (HHV)	71 %	81 %
AC to H_2 efficiency (LHV)	60 %	69 %

Saarinen, V., Pennanen, J., Kotisaari, M., Thomann, O., Himanen, O., Iorio, S. D., Hanoux, P., Aicart, J., Couturier, K., Sun, X., Chen, M., & Sudireddy, B. R. (2021). Design, manufacturing, and operation of movable 2 × 10 kW size rSOC system. Fuel Cells, 21(5), 477-487. https://doi.org/10.1002/fuce.20210002

Outlet molar fractions and H_2/CO ratio as a function of inlet CO_2 molar fraction (i=0.2 A/cm^2)



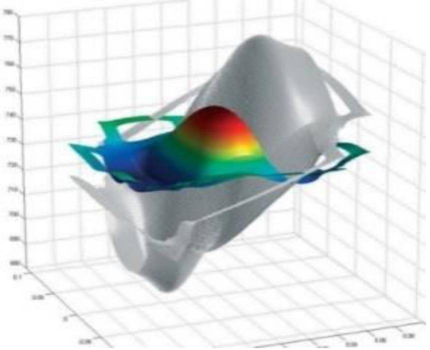


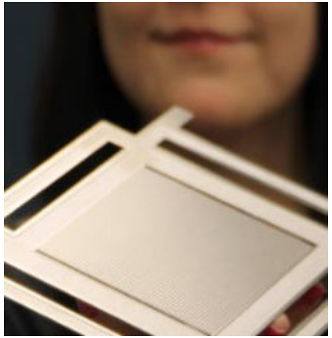
Summary

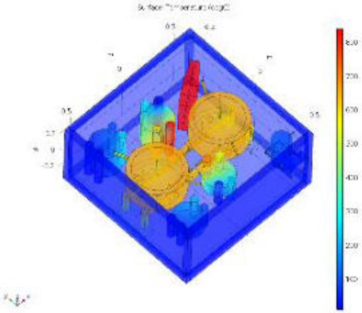
- High temperature electrolysis (SOEC) can produce hydrogen or syngas with high efficiency (80-90%) and utilise waste heat, which enables more efficient power-to-X, if integrating SOEC as part of industrial processes
- SOEC technology is reversible: the same system can work both as a fuel cell and an electrolyser depending on power generation and grid stabilisation needs
- Movable “10-foot container” size Reversible Solid Oxide Cell (rSOC) system has been designed and developed in pilot demonstration scale at VTT
- Wide range of operation parameters were tested to achieve eligible outlet gas composition (H_2 / CO = 2) suitable for upstream FT-synthesis

Thank you for your attention. Any questions?

D.Sc (Tech.) Ville Saarinen ville.saarinen@vtt.fi +358 40 620 2933







LUT
University

LAND OF THE CURIOUS

KEROGREEN WINTER SCHOOL, 10-11.2.2022

‘’DYNAMIC ENERGY AND MASS BALANCE MODEL FOR AN INDUSTRIAL ALKALINE WATER ELECTROLYZER PLANT PROCESS.”

Sakas, G., Ibáñez-Rioja, A., Ruuskanen, V., Kosonen, A., Ahola, J. and Bergmann, O., 2022. Dynamic energy and mass balance model for an industrial alkaline water electrolyzer plant process. *International Journal of Hydrogen Energy*, 47(7), pp.4328-4345.

Presenter: Georgios Sakas, Junior Researcher, LUT University

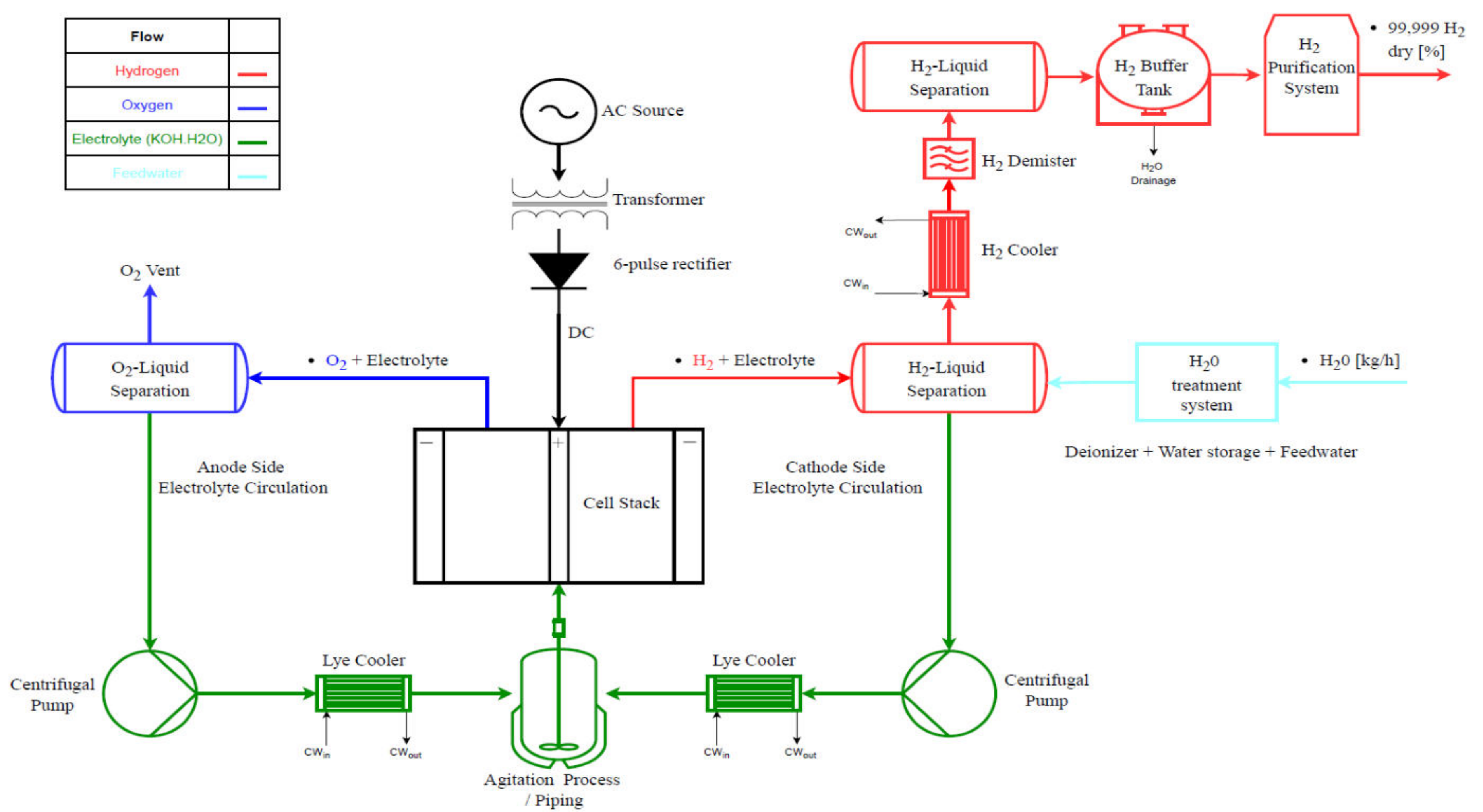
HIGHLIGHTS OF THE ARTICLE

1. Large-scale simulation of a 3 MW, 16 bar industrial alkaline water electrolyzer was developed in MATLAB Simulink.
2. Mass and energy balances were verified and adjusted with measurements from an operating plant of similar size and type.
3. Steady-state analysis showed Faraday efficiency of 86%.
4. 96% of the generated heat was extracted from the heat exchangers.
5. Contribution of each Faraday loss parameter was approximated for a steady-state case.

» **Simulation/Model objectives:**

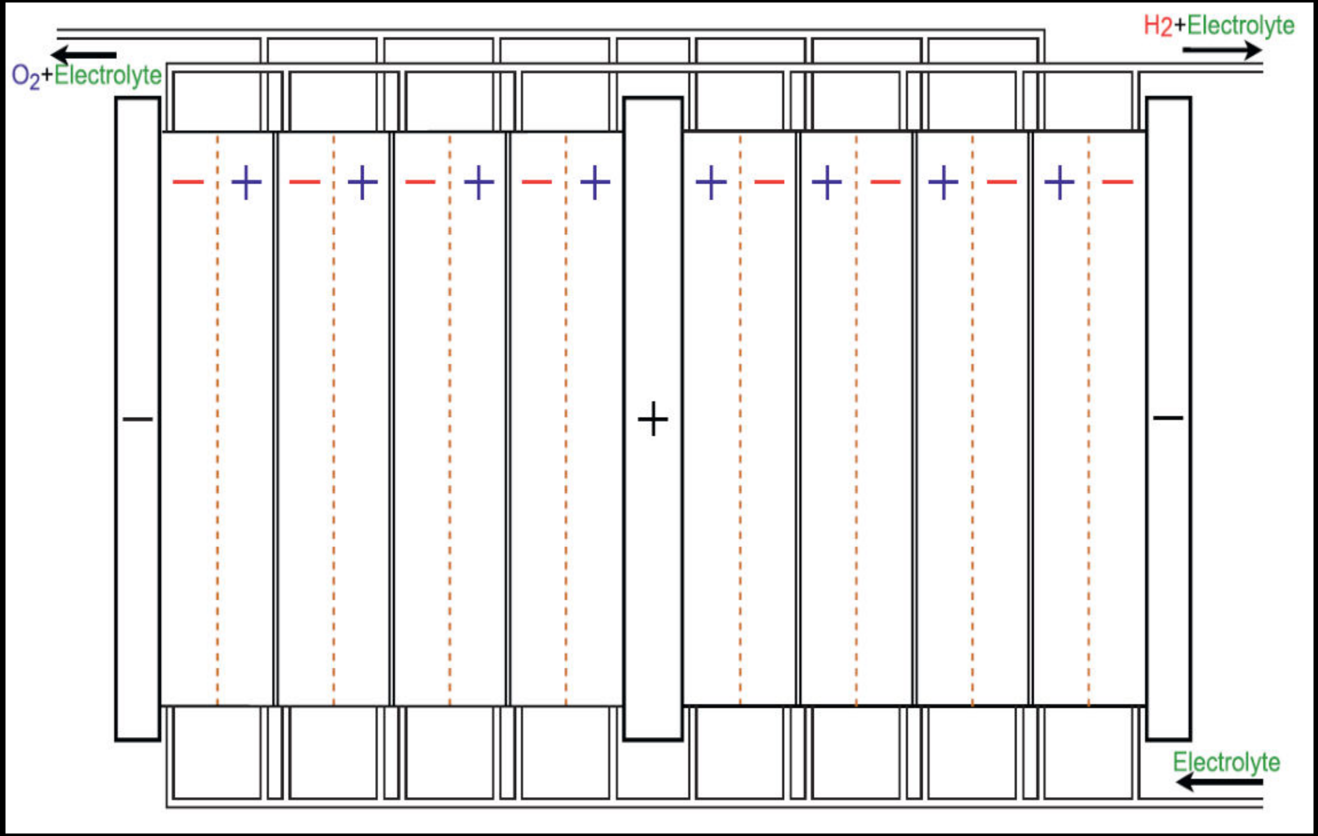
1. Determine the important peripheral components.
    - Most potential for improvements
2. Optimize the performance of each component individually.
    - Energy loss.

PID DIAGRAM – THEORY



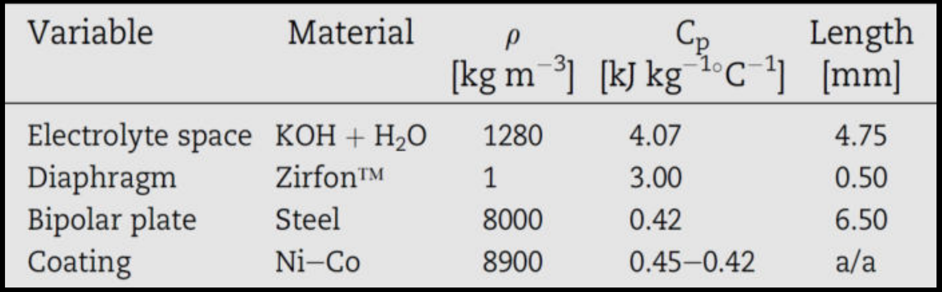
- Various real industrial cases were investigated.
- Blueprint.
- System to be simulated.

ELECTROLYZER STACK DESIGN (BIPOLAR CONFIGURATION)



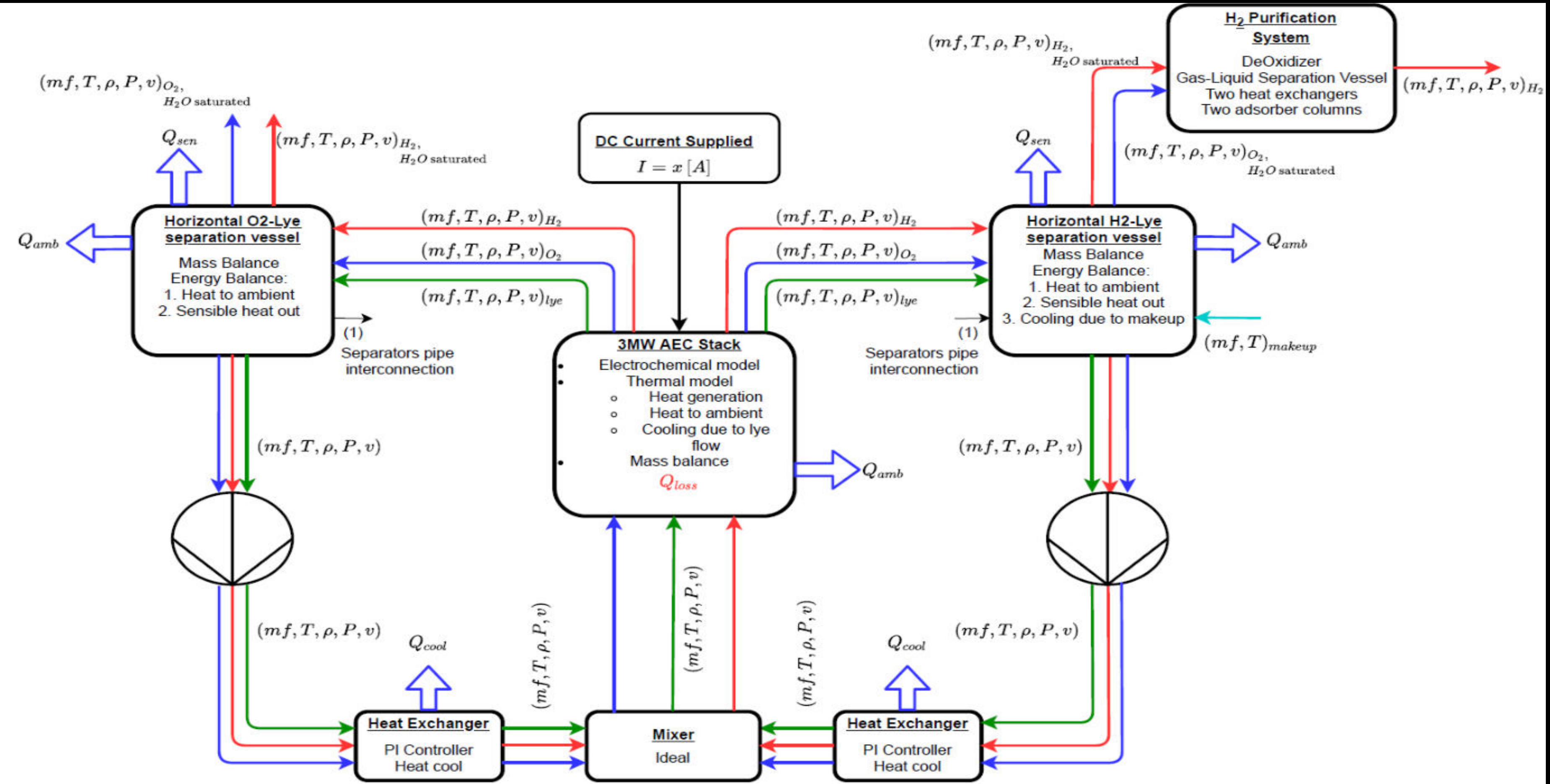
- $A_{\text{cell}} = 2.66\,m^2$
- $N_{\text{c}} = 326$
- $N_{\text{c,series}} = 163$
- Two half stacks connected in parallel.

Table 1 – Engineering design of each modelled electrolyzer cell.



Variable	Material	ρ [kg m^{-3}]	C_p [kJ kg^{-1}°C^{-1}]	Length [mm]
Electrolyte space	KOH + H_2O	1280	4.07	4.75
Diaphragm	Zirfon™	1	3.00	0.50
Bipolar plate	Steel	8000	0.42	6.50
Coating	Ni–Co	8900	0.45–0.42	a/a

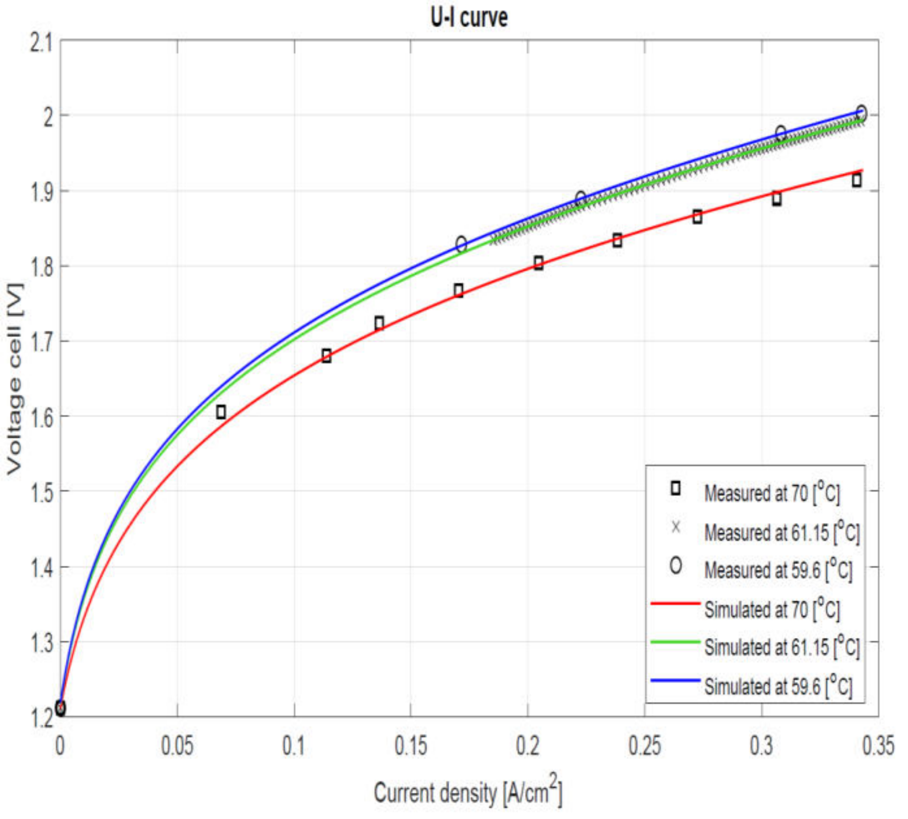
SIMULINK DIAGRAM



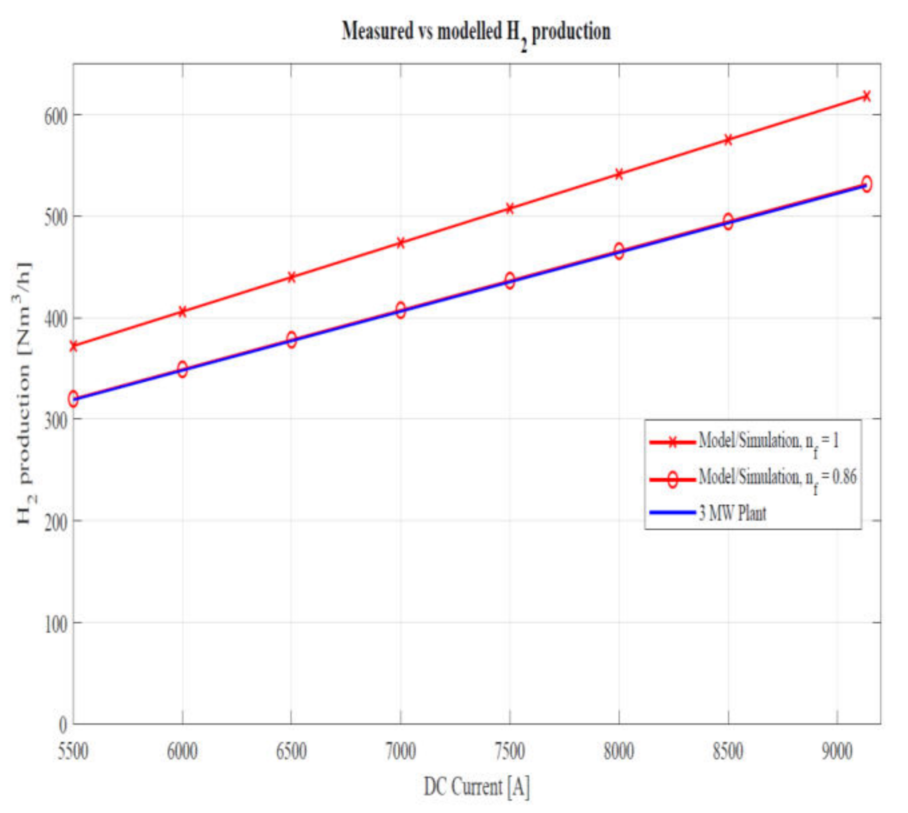
- Matlab function Simulink block for each unit operation.
- Signal flow:
  - Output from one unit operation.
  - Input to the next one.
- Vector Signals:
  - Mass flow
  - Temperature
  - Density
  - Pressure
  - Voidage
- Main model parameter:
  - DC Current supplied to the stack per second.

Current investigation: How can we re-dimension and run the plant to reduce the H_2 cost? (based on minimum SEC).

RESULT (1): ELECTROCHEMICAL MODEL; POLARIZATION CURVE, FARADAY EFFICIENCY.

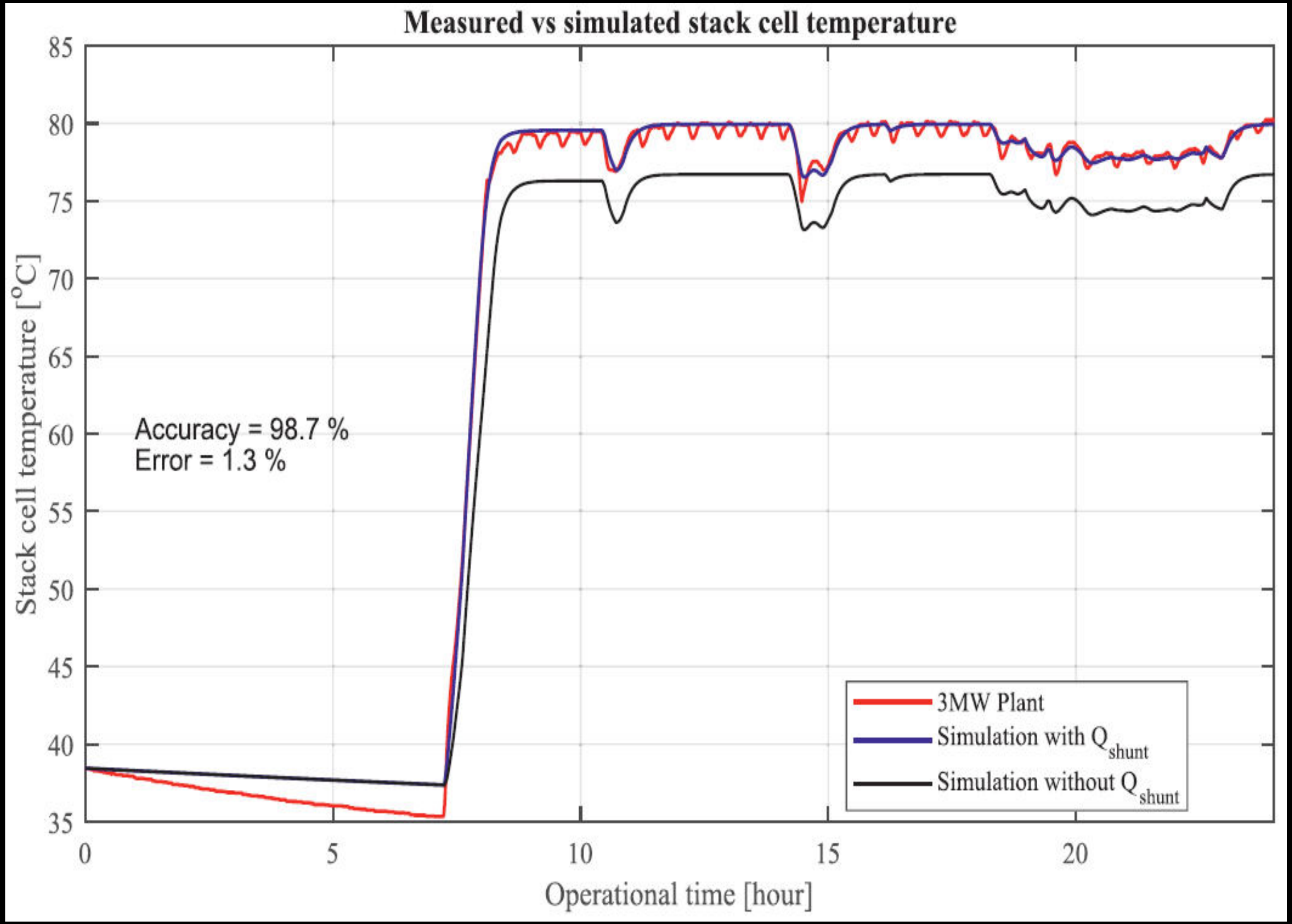


Curve fitting with measurements taken from the industrial 3MW stack.



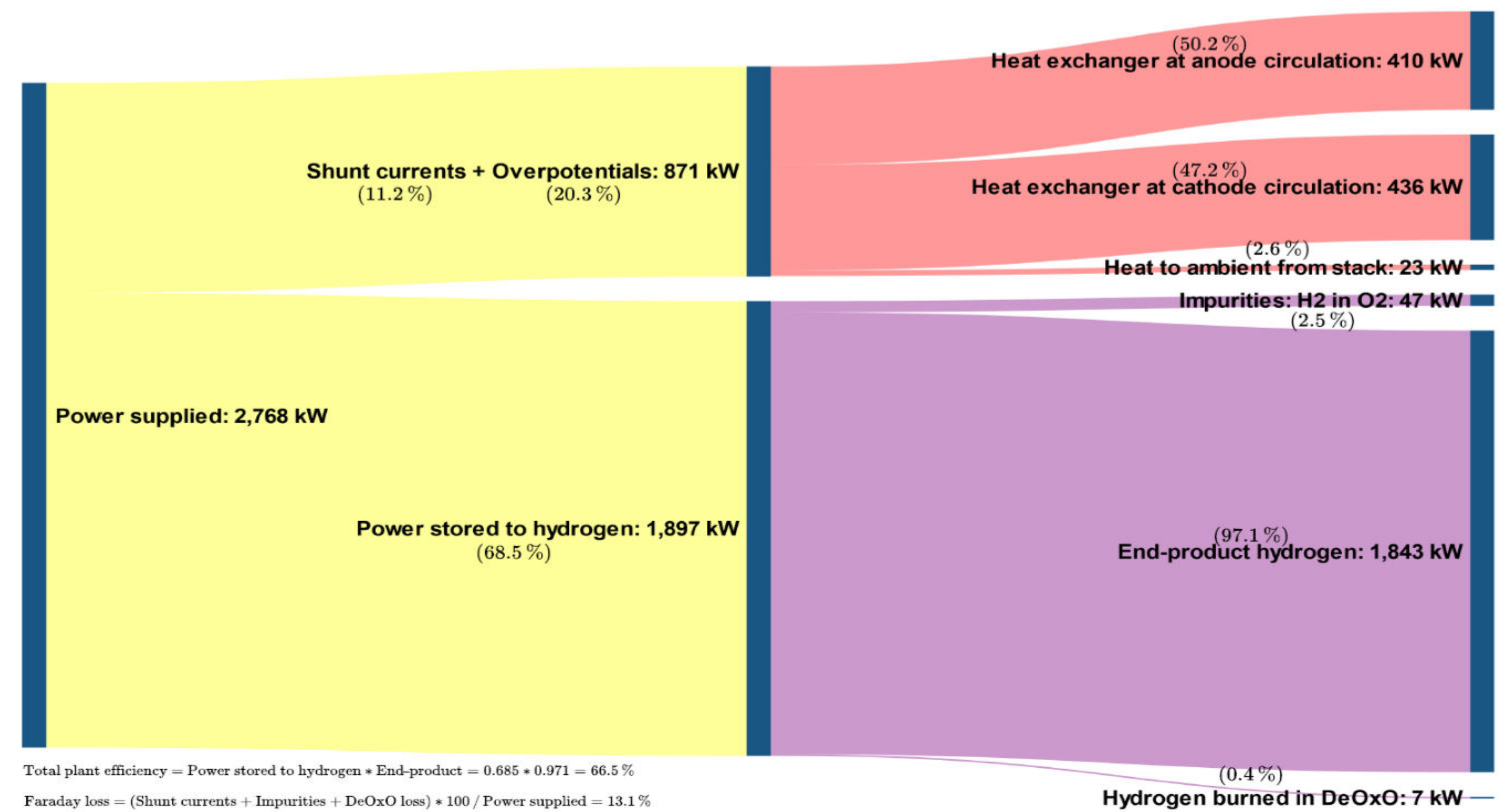
The model behavior matched the plant at 86% Faraday efficiency, i.e., 14% of the current efficiency is lost to side reactions.

RESULT (2) THERMAL MODEL; SHUNT CURRENTS



- Verification of energy balance:
  - Same behavior of temperature phenomena.
  - Very small differences in time variation.
- Dissipated heat due to shunt currents:
  - Thermal model converged at 308 kW of shunt currents power loss.
  - 11.2% of the estimated 14% Faraday loss.
  - Common issue in bipolar configurations.
- Reliable steady-state results.

RESULT (3): STEADY-STATE ANALYSIS; POWER CONSUMPTION.



Total plant efficiency = Power stored to hydrogen ∗ End-product = 0.685 ∗ 0.971 = 66.5 %

Faraday loss = (Shunt currents + Impurities + DeOxO loss) ∗ 100 / Power supplied = 13.1 %

- From the total power input: 20.3% Overpotentials + 11.2% Shunt currents
  - Heat generated:
    - 97.4% removed from heat exchangers.
    - 2.6% from stack to
- 68.5% of the total power input is converted to hydrogen:
  - 2.5% of the produced hydrogen is lost as impurities in the opposite cell: diaphragm diffusion + gas dissolution in the circulation.
  - 0.4% of the produced hydrogen is burned in DeOxidizer to remove the oxygen impurities.
  - 97.1% of produced hydrogen is the final product.

Thank you!
Questions?

LUT University

P2X ENABLE

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

Syngas Production in the Kerogreen Process Chain:

Development of a compact Sorption-Enhanced Water-Gas Shift Reactor

T.J. Stadler, P. Pfeifer
Karlsruhe Institute of Technology

Kerogreen Winter School, 10.-11.02.2022, virtual event

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

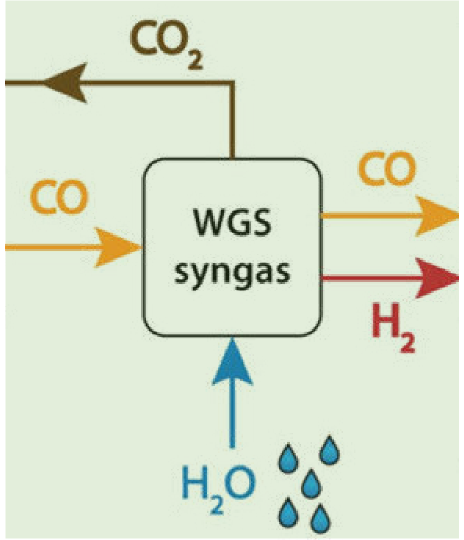
Synthesis Gas Production from pure CO

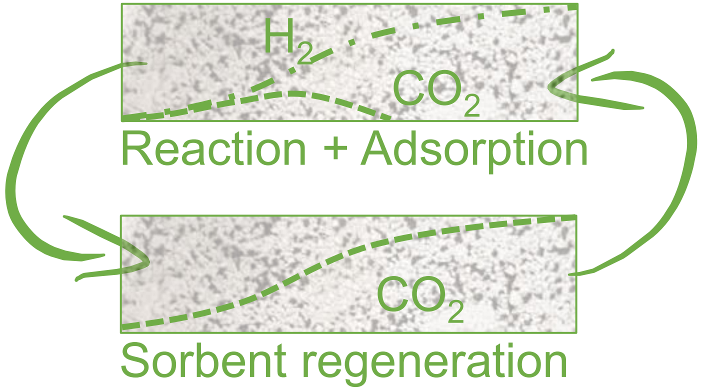
- Approach: Sorption-enhanced water-gas shift reaction (SEWGS)

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_R^0 = -41.1\ \mathrm{kJ/mol}$$

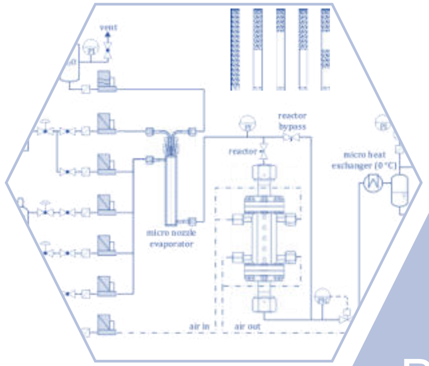
- H_2:CO ~ 2 for subsequent F-T synthesis
- CO_2 removal for recycle to plasmolysis unit

- Fixed-bed reactor system
  - CO_2 sorbent
  - WGS catalyst
- Cyclic operation
  - CO_2 adsorption during WGS
  - Sorbent regeneration with steam and N_2



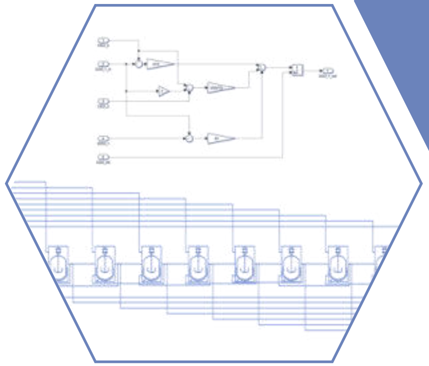


- Time and space dependent process → **simulation-driven design and development**



SEWGS:

Breakthrough Experiments

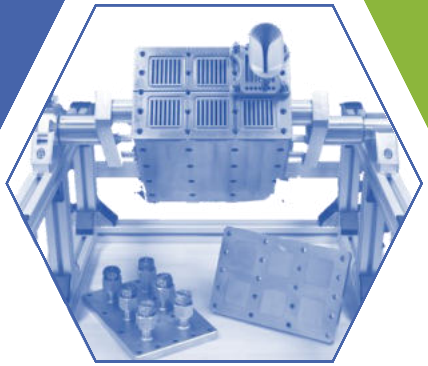


SEWGS:

Modeling and Simulation

SEWGS:

Pilot Plant Module



FT-HC:

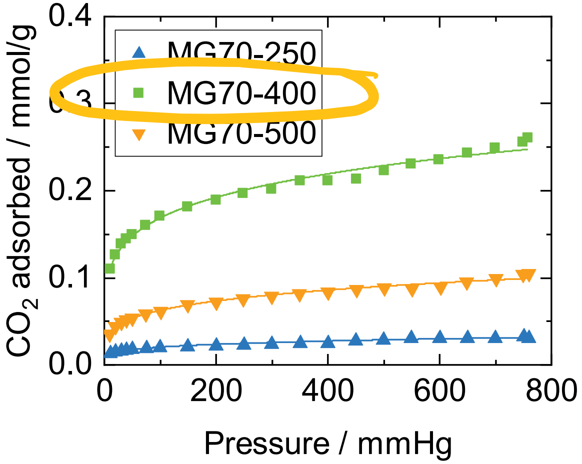
Impact of CO_2

Lab-Scale: Choice of Materials

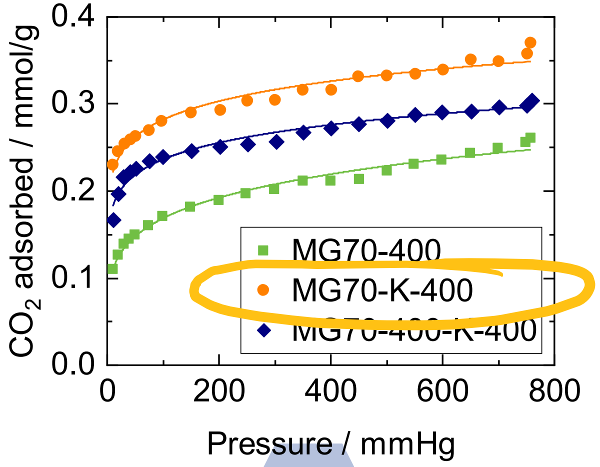
- Catalyst
  - Low-temperature WGS catalyst (200 – 300 °C)
  - Commercial Cu/ZnO-Al_2O_3 pellets

- Sorbent
  - Potassium-impregnated hydrotalcite
  - Chemisorption isotherms @250 °C:

Calcination temperature

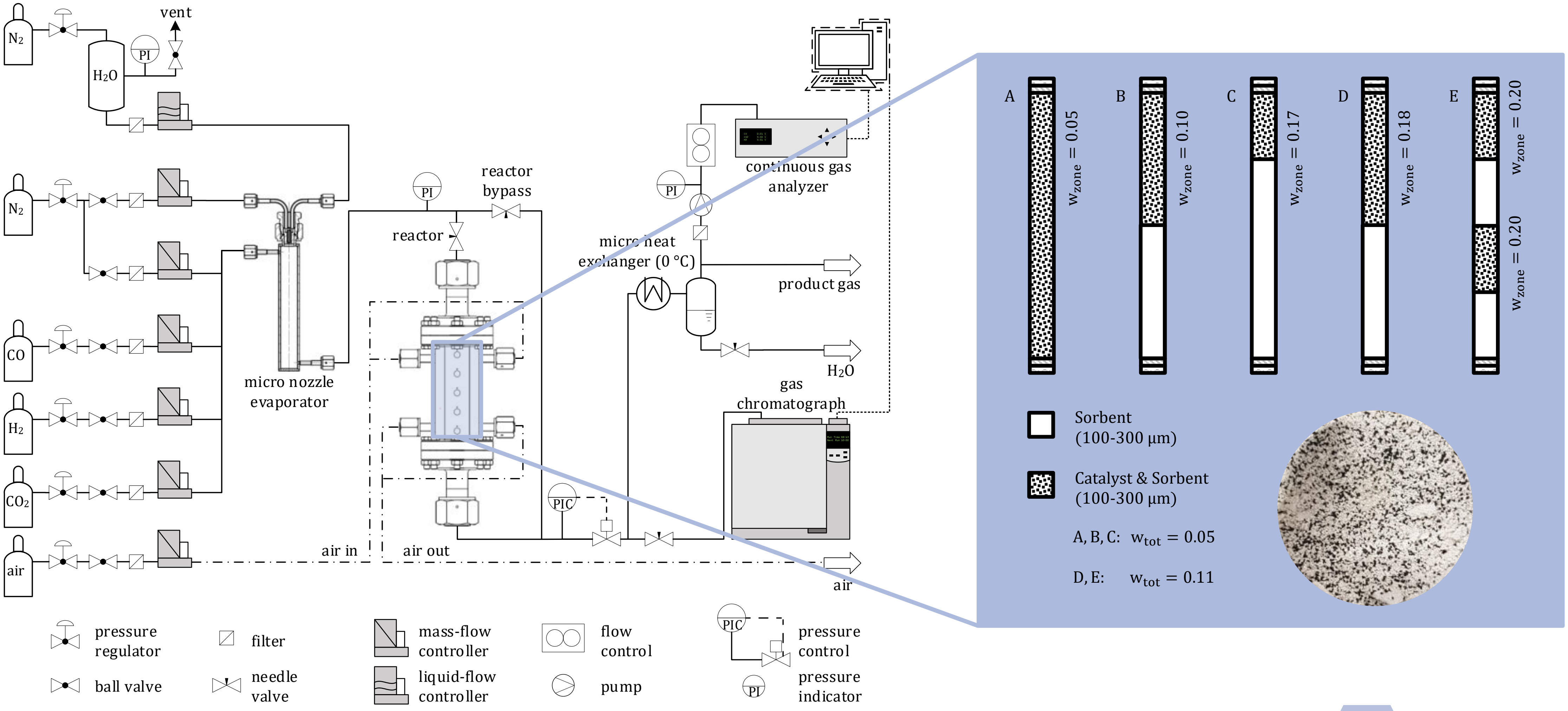


Impregnation procedure



[Stadler, T. (2021). Sorption-Enhanced Water-Gas Shift Reaction for Synthesis Gas Production from Pure CO. Energies 14 (2), 355. doi:10.3390/en14020355.]

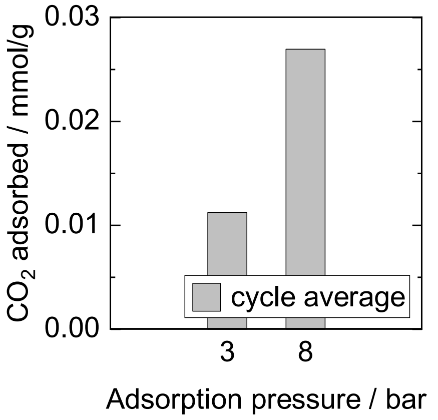
Lab-Scale: Choice of Process Conditions

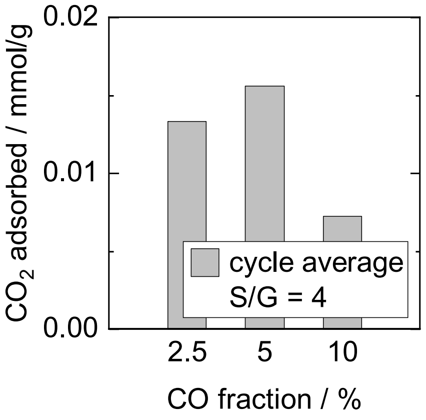


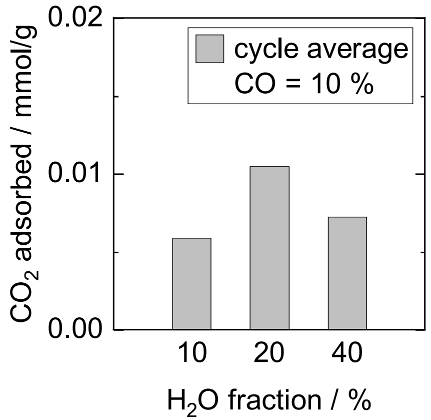
[Stadler, T. (2021). Sorption-Enhanced Water-Gas Shift Reaction for Synthesis Gas Production from Pure CO. Energies 14 (2), 355. doi:10.3390/en14020355.]

Lab-Scale: Choice of Process Conditions

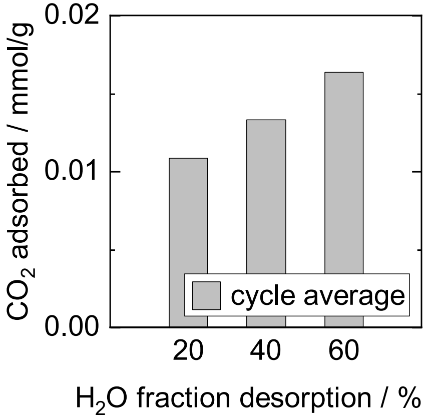
Adsorption parameters

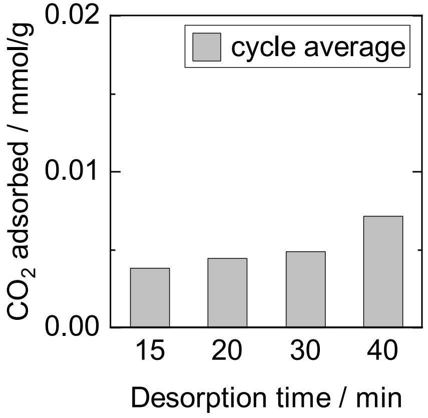




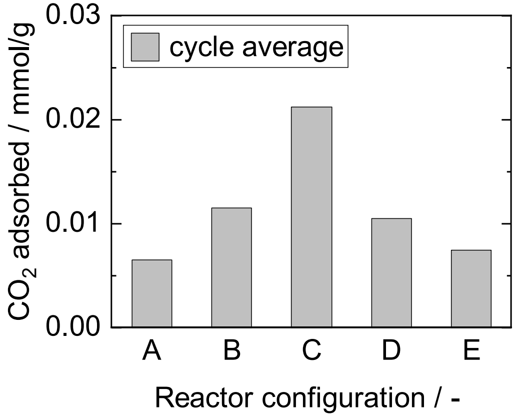


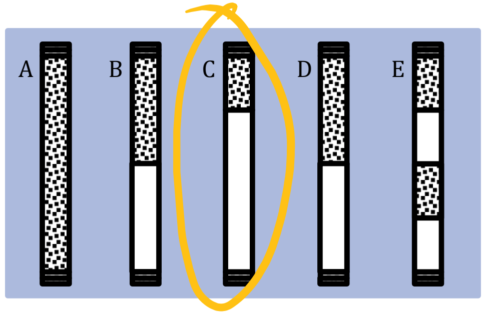
Desorption parameters





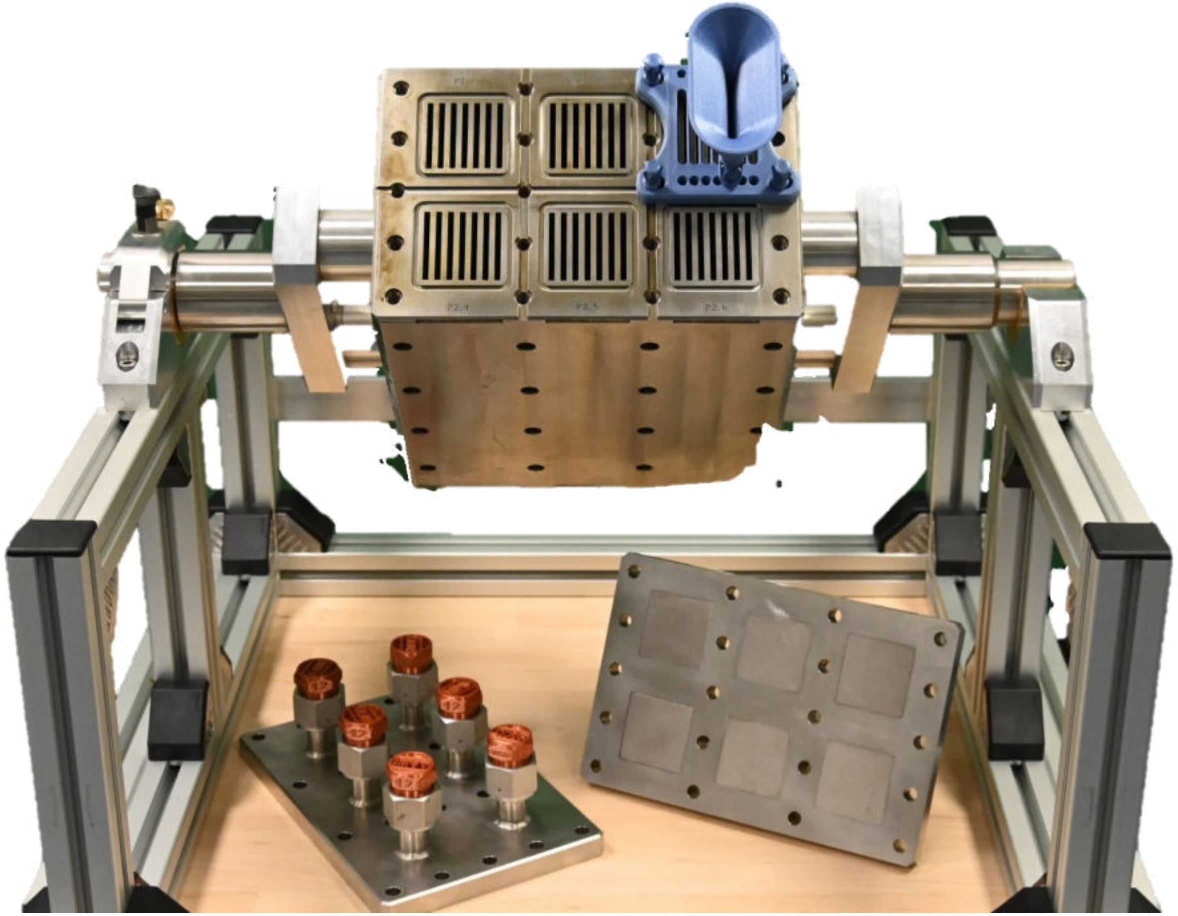
Reactor configuration





[Stadler, T. (2021). Sorption-Enhanced Water-Gas Shift Reaction for Synthesis Gas Production from Pure CO. Energies 14 (2), 355. doi:10.3390/en14020355.]

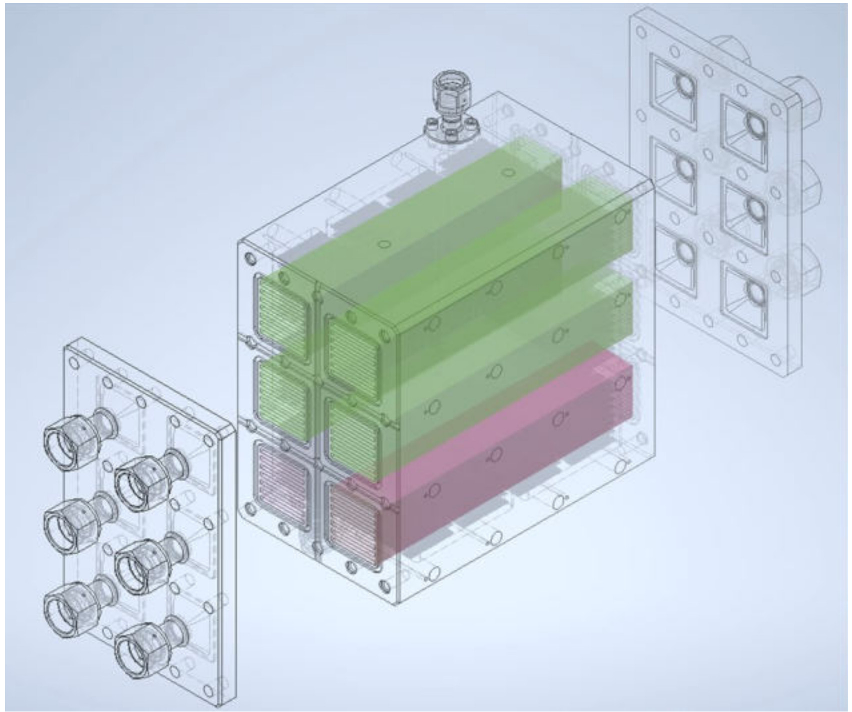
Scale-Up: Pilot Plant Reactor Design



- SEWGS reactor
  - Compact layout (290x310x190 mm)
  - One diffusion-bonded apparatus
- Gas flow
  - Six individually fed reaction chambers
  - Each consists of seven slits
  - Slits filled with sorbent and catalyst
- Temperature control
  - Heating Cartridges
  - Adjacent channels between the slits for T control

Scale-Up: SEWGS Module Integration

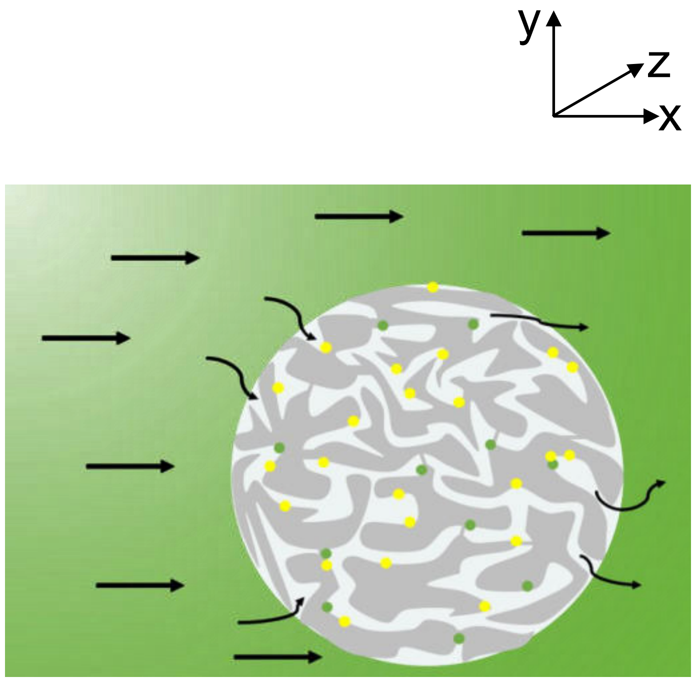
- SEWGS module in container-sized pilot plant
- Simulation-driven plant operation concepts



Process Simulation: Model Development

- Time and space (z-direction) resolved

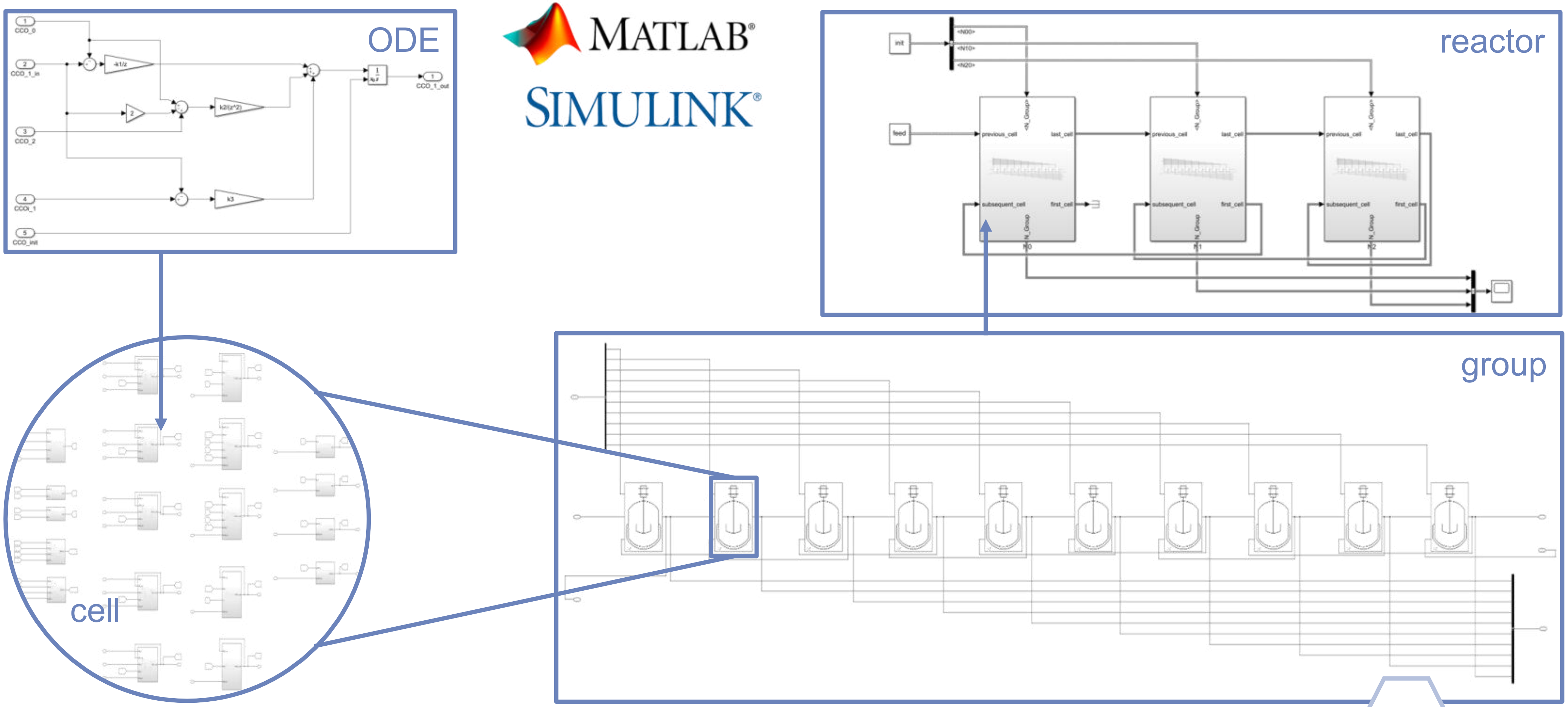
- Rectangular channel filled with sorbent and catalyst
    - Isothermal system: reactor design
    - Isobaric system: Δp negligible
    - No dispersion in x,y-direction: $d_{bed}/d_{particle} > 10$
    - Mass transport limitations
        - External (Maers): negligible
        - Intraparticle (Weisz-Prater): not negligible



- Heterogeneous reactor model
    - WGS reaction kinetics [1]
    - Adsorption kinetics of CO_2 and H_2O on 3 sorption sites [2]
    - Desorption kinetics based on equilibrium

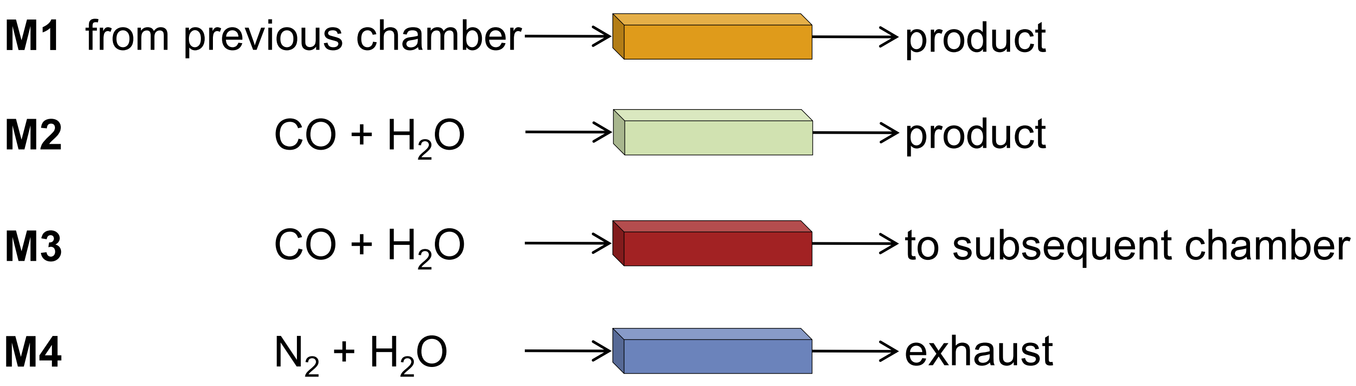
[1] Choi, Y. (2003). Water gas shift reaction kinetics and reactor modeling for fuel cell grade hydrogen. J. Power Sources 124 (2), 432-439. doi:10.1016/S0378-7753(03)00614-1.
[2] Coenen, K (2019). Kinetic model for adsorption and desorption of H_2O and CO_2 on hydrotalcite-based adsorbents. Chem. Eng. J. 355, 520-531. doi:10.1016/j.cej.2018.08.175.

Process Simulation: Hierarchical Reactor Model



[Stadler, T. (2022). Numerical Simulation Approach for a Periodically Operated Sorption-Enhanced Water-Gas Shift Reactor. Submitted.]

Process Simulation: Cyclic Operation

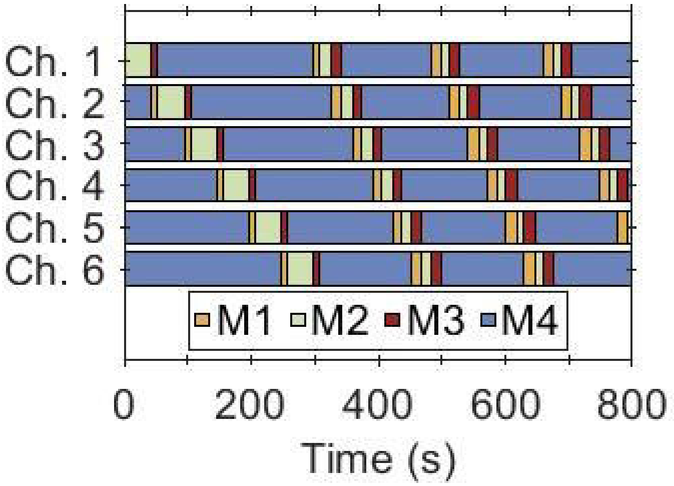


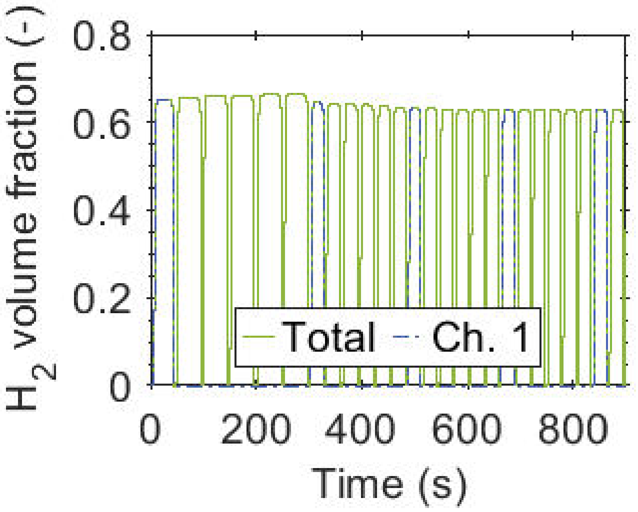
M1 from previous chamber → product

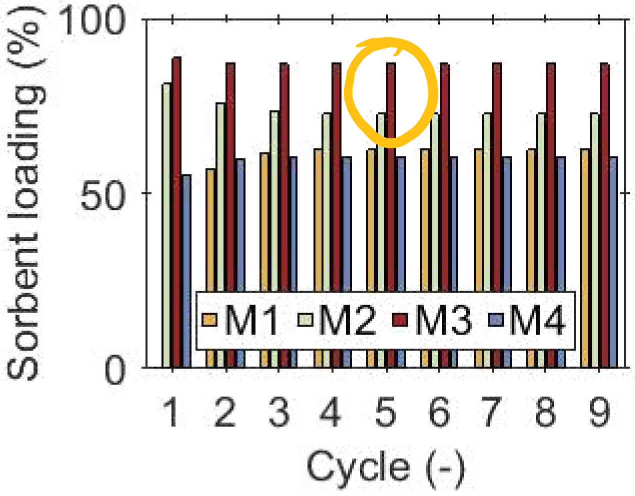
M2 CO + H_2O → product

M3 CO + H_2O → to subsequent chamber

M4 N_2 + H_2O → exhaust





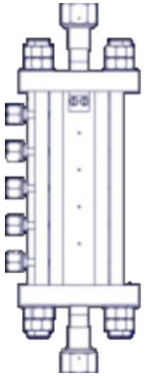


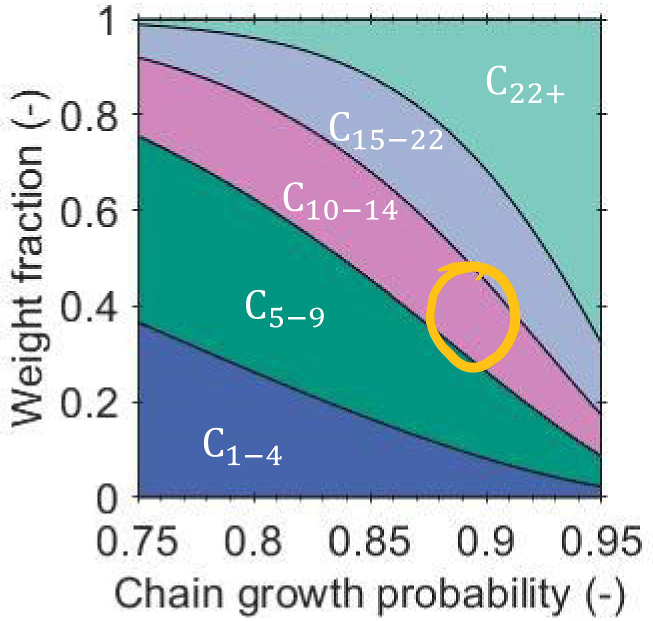
- Continuous CO_2-free H_2 production
- Increased sorbent usage (15 %) due to interconnected chambers
- Automatically adjusted switching times

[Stadler, T. (2022). Numerical Simulation Approach for a Periodically Operated Sorption-Enhanced Water-Gas Shift Reactor. Submitted.]

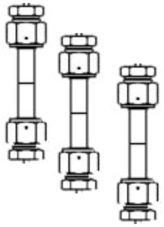
Influence of SEWGS performance on FT-HC step

- Fischer-Tropsch Synthesis (FT)
  - Alkanes: $n\ \mathrm{CO} + (2n+1)\ \mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\ \mathrm{H_2O} \quad \Delta H_\mathrm{R} < 0$
  - Alkenes: $n\ \mathrm{CO} + (2n)\ \mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\ \mathrm{H_2O}$
  - Alcohols, other oxygenates, …
  - Micro-structured reactor
  - Co-based catalyst





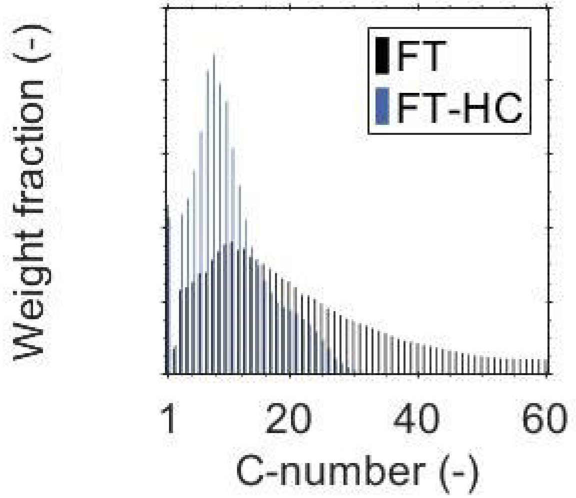
- Hydrocracking (HC)
  - Cracking: $\mathrm{C}_n\mathrm{H}_{2n+2} \rightarrow \mathrm{C}_{n-m}\mathrm{H}_{2(n-m)} + \mathrm{C}_m\mathrm{H}_{2m+2} \quad \Delta H_\mathrm{R} > 0$
  - (De)hydrogenation: $\mathrm{C}_{n-m}\mathrm{H}_{2(n-m)} + \mathrm{H_2} \rightleftharpoons \mathrm{C}_{n-m}\mathrm{H}_{2(n-m)+2} \quad \Delta H_\mathrm{R} > 0$
  - Reactor cascade
  - Bifunctional Pt-ZSM5 catalyst

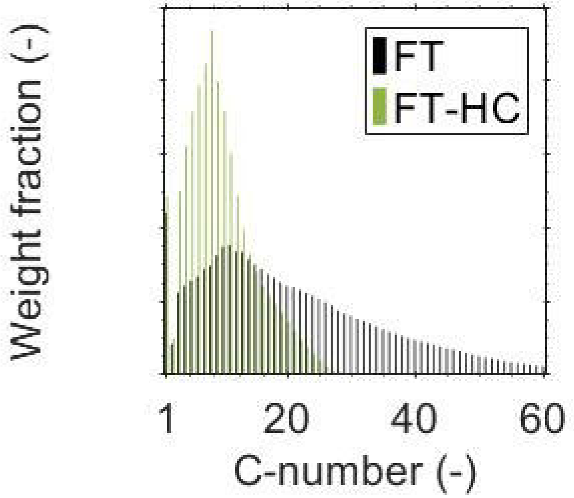


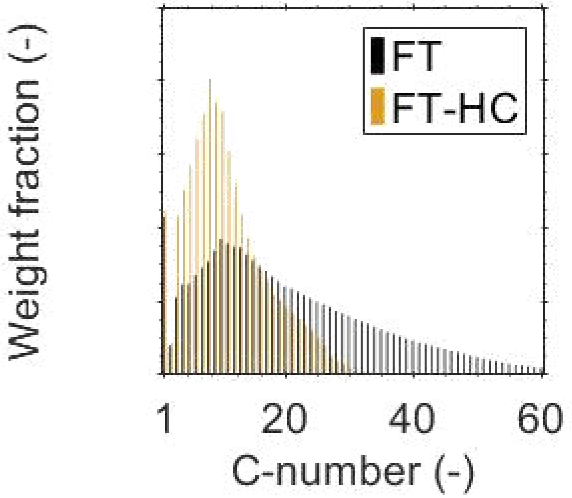
[Stadler, T. (2022). Influence of CO_2-Rich Syngas on the Selectivity to C_{10}–C_{14} in a Coupled Fischer-Tropsch/Hydrocracking Process. Chem. Ing. Tech. 94 (3). doi:10.1002/cite.202100172.]

Influence of SEWGS performance on FT-HC step

- Synthesis gas (FT feed): no CO_2 separation, partly CO_2 separation in SEWGS


40 % N_2

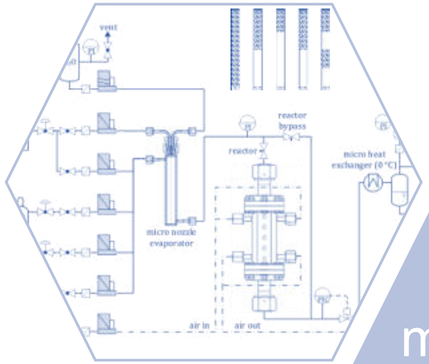

40 % CO_2


5 % CO_2 + 35 % N2

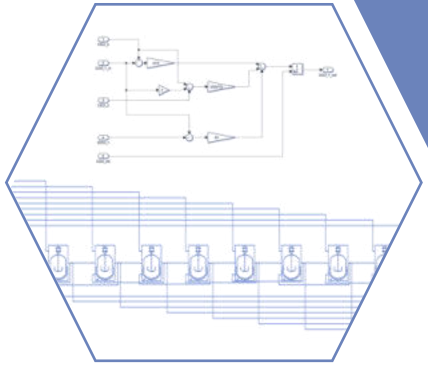
- Net production of hydrocarbons in HC is strictly limited to C_{14}
- CO_2 acts as diluent with regard to reaction on the HC catalyst
- Diluting effect of CO_2 has to be considered

[Stadler, T. (2022). Influence of CO_2-Rich Syngas on the Selectivity to C_{10}–C_{14} in a Coupled Fischer-Tropsch/Hydrocracking Process. Chem. Ing. Tech. 94 (3). doi:10.1002/cite.202100172.]

Conclusions and Outlook

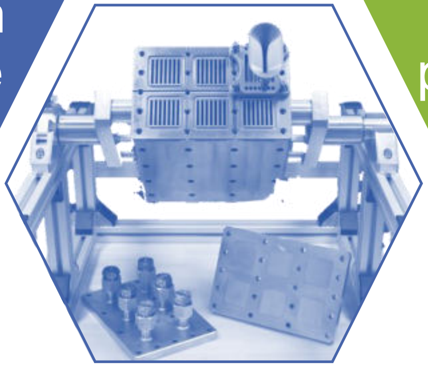


Suitable materials and process conditions



Hybrid model for intensified plant operation

In-house built reactor integrated in pilot module



Limited influence on subsequent process step

Cyclic SEWGS process operation test in pilot-plant

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Karlsruhe Institute of Technology (KIT)
Institute for Micro Process Engineering (IMVT)

Thank you for your attention!

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

E-FUEL

Co-electrolysis with FT

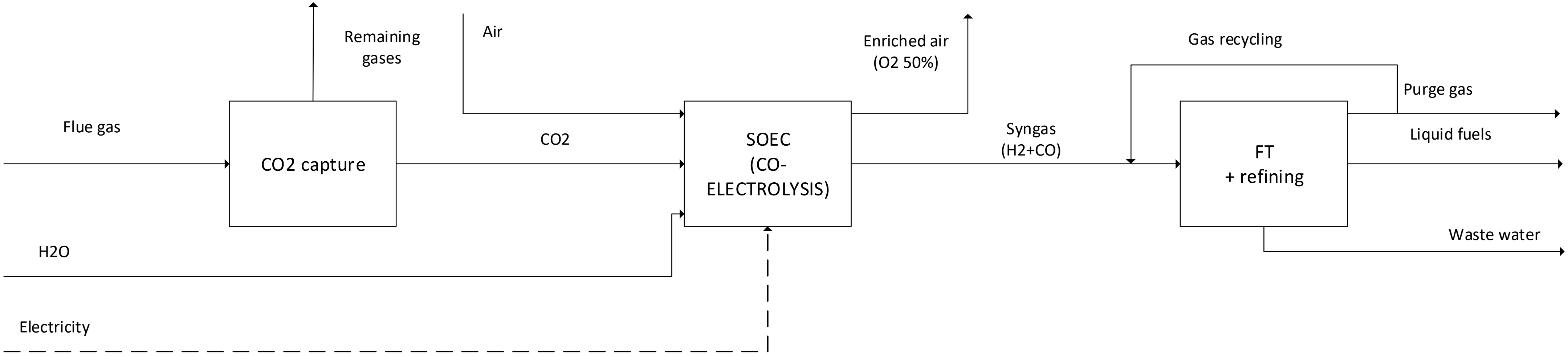
Techno-economic assessment

Winter school 10.02.2022

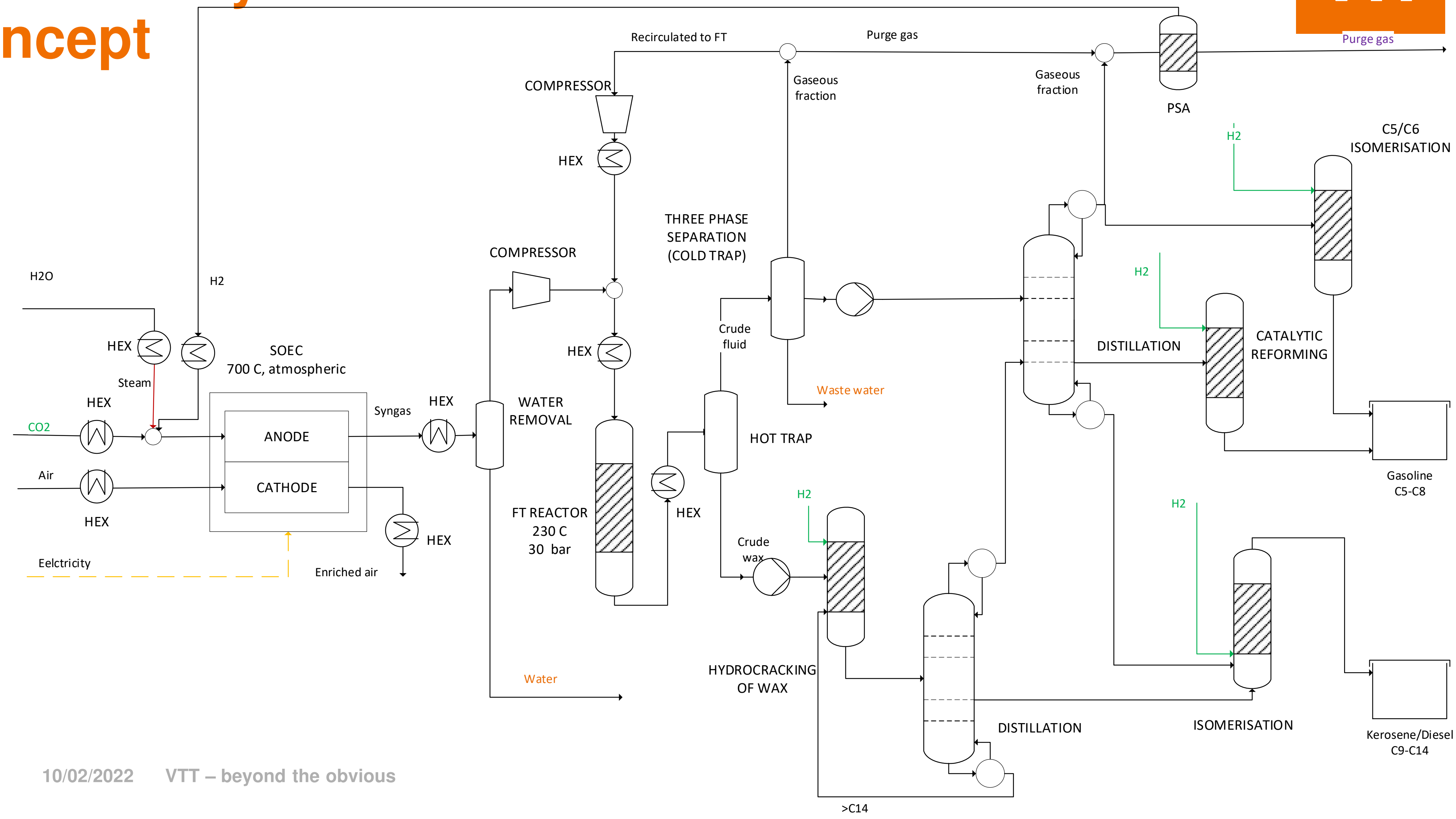
Marjut Suomalainen, Miia Nevander,
Markus Hurskainen

Efuel production via co-electrolysis and FT

- Production cost estimate for target products diesel /jet fuel
- Target in large scale operation around 2030
- By-product gasoline
- Flue gas input 315 t/h
  - source power plants or process heat generation (CO_2 content 20 wt%)
  - capture method amine-based absorption (monoethanolamine, MEA)



Co-electrolysis +FT concept

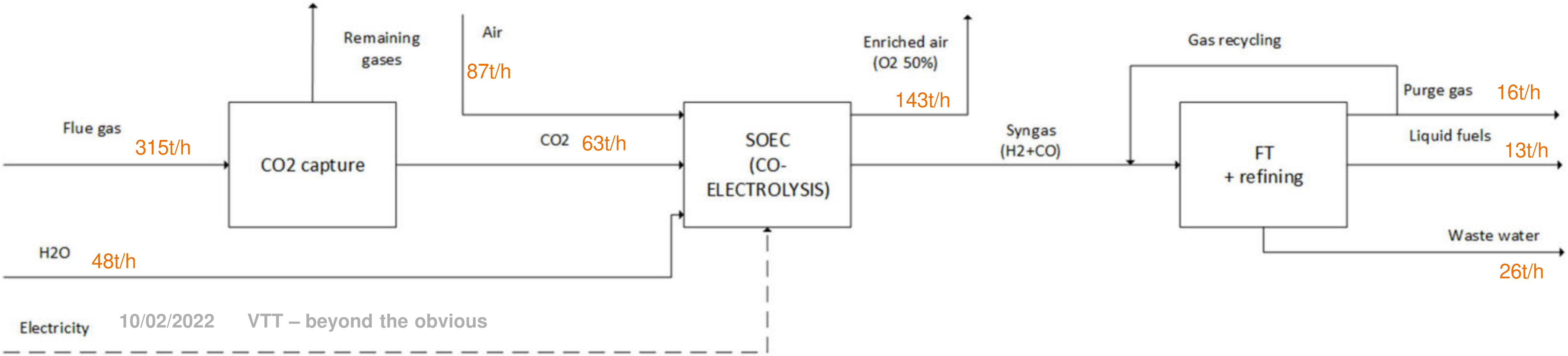


Main technical parameters

- Steady-state modelling using Aspen Plus simulation software
- CO_2 absorption by MEA
  - Stream to co-electrolysis 63 t/h of which
    - CO_2 99 wt%
    - H_2O 1 wt%
    - Minor amount of N_2 and O_2
- Co-electrolysis
  - 0d model of cross flow electrolyser, operation temperature 700 ^oC
  - Faradic loss 1%, heat loss 2%, area specific resistance (ASR) 0.5 ohm*cm^2
  - AC/DC efficiency 90%
  - Electrical efficiency 90% for heating gases from 650 to 700 ^oC
  - Hydrogen input 5 mol% of total CO_2, H_2O, and H_2 input
  - Current density (i) 0.8 A/cm2
- FT reactor (Co catalyst):
  - stoichiometric reactions for formation of alkanes up to C_{30} and alkenes up to C_{20}
  - Alpha for product distribution 0.93
  - Ratio H_2/CO =2.0
  - Once through CO conversion 0.75
  - Gas recycling rate 60%
- Refining section
  - Modelling based on real components
  - Lumping and simplifying hydrocracking reactions
    - H_2 consumption calculated
  - Currently no detailed modelling for catalytic reformer and isomerisation
    - H_2 consumption estimated based on literature
- PSA for hydrogen production
  - H2 recovery 92%
  - Vacuum 0.1 bar

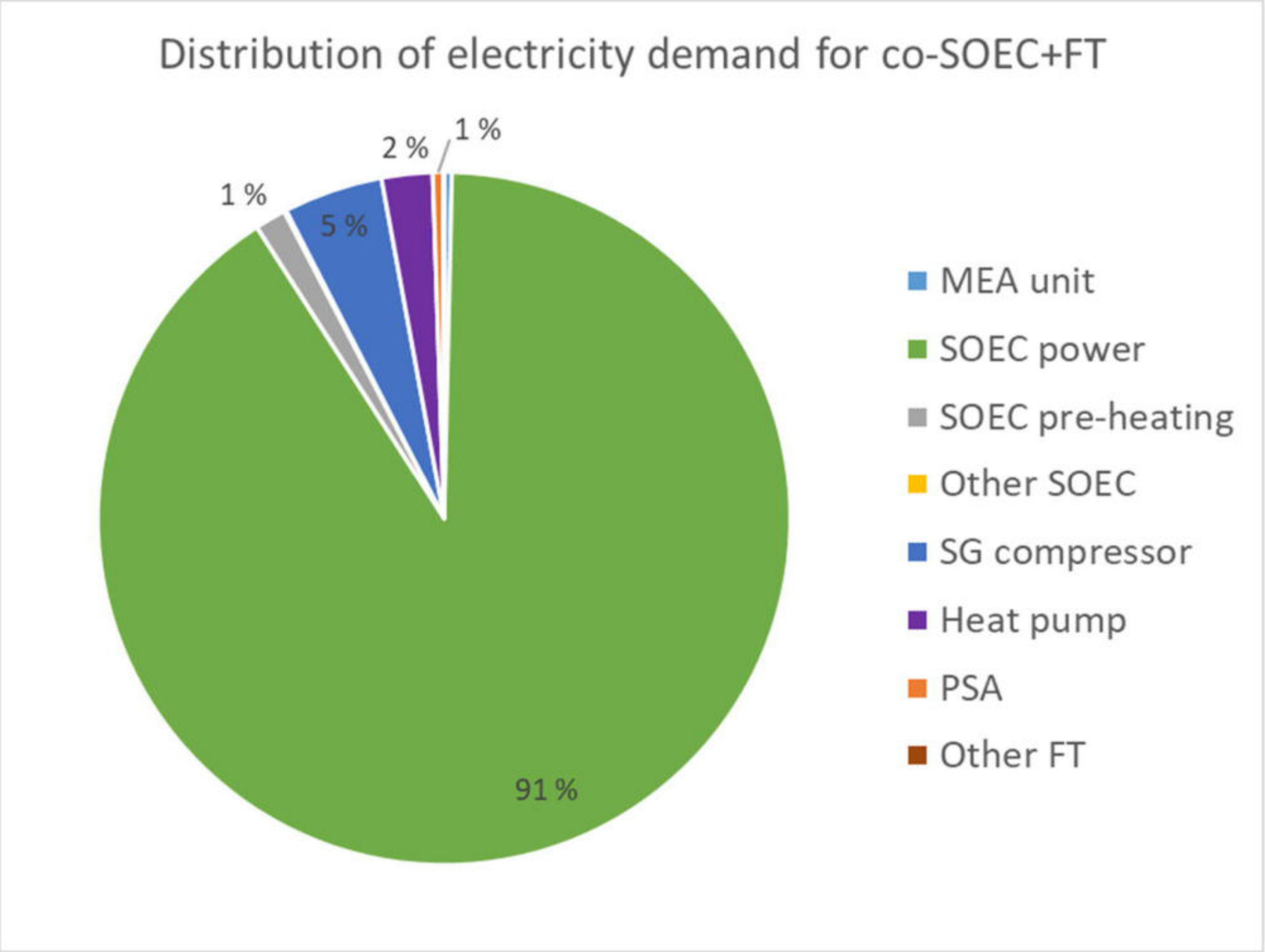
Mass balance and performance

- Production
  - Diesel 7.5 t/a
  - Gasoline 6.0 t/h
- Co-SOEC
  - Reactant utilisation 84%
  - Vcell 1.35 V
  - Electrical efficiency to syngas 85% (LHV)
- Electricity consumption 310 MW
  - Electricity to liquid fuels 48%
- Heat integration
  - No additional heat required
  - District heating potential 55 MW (120-70 C) based on pinch analysis, applying heat pump for low grade heat



Electricity demand

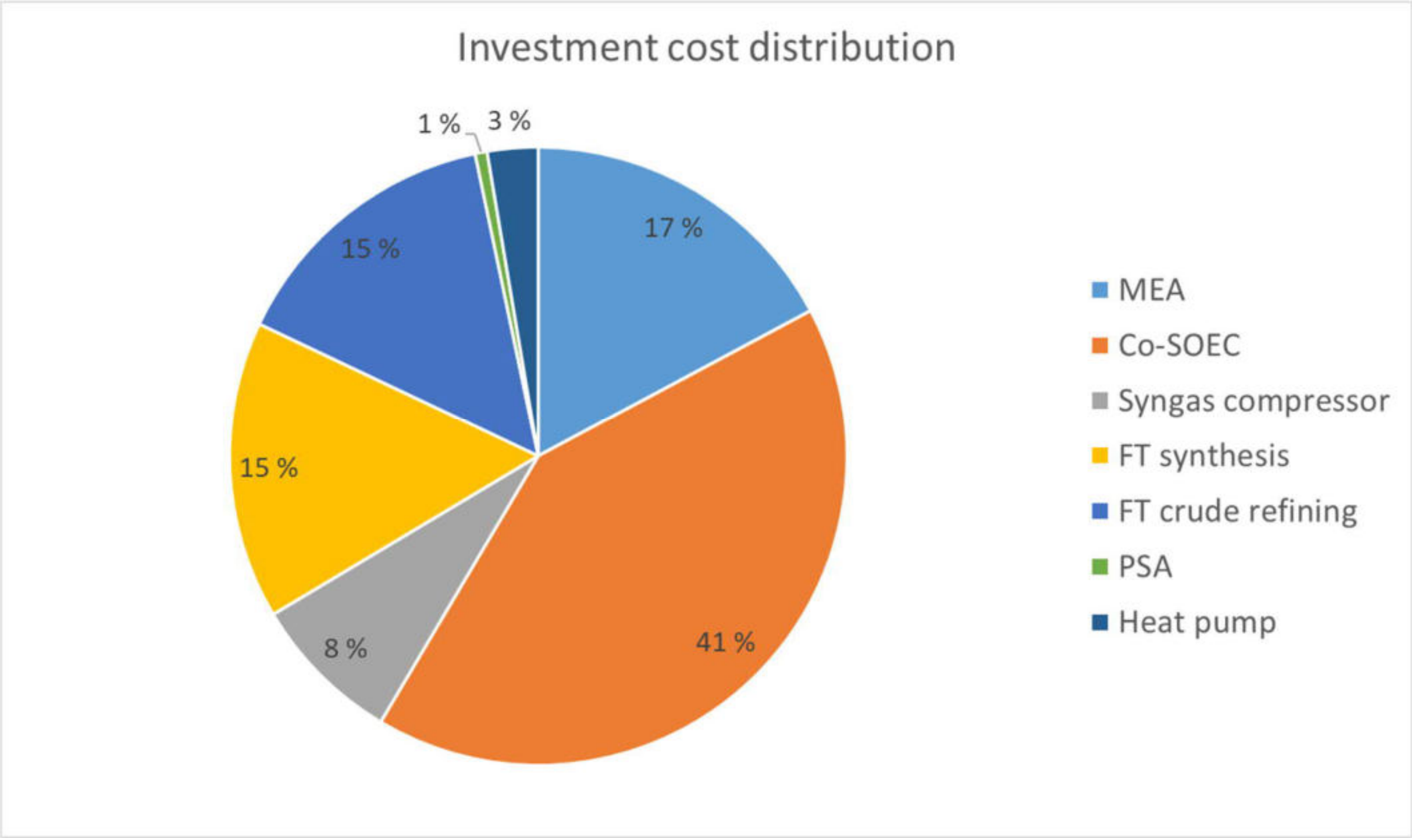
- Electricity demand 310 MW
- SOEC electrical efficiency to syngas 85% LHV
- Electricity to liquid fuels 48%



Preliminary CAPEX estimate

- Plant capacity
  - SOEC 290 MW
  - CO_2 in 63 t/h
  - Liquid fuels 100 000 t/a

- Total CAPEX 550 M€
  - Of which SOEC 230 M€ (based on 800 €/kWe)



Assumptions related to operation costs, product prices and financial parameters

- Annual operation 8322 h/a
  - (95%)
- Investment subsidy not considered
- Insurance not included

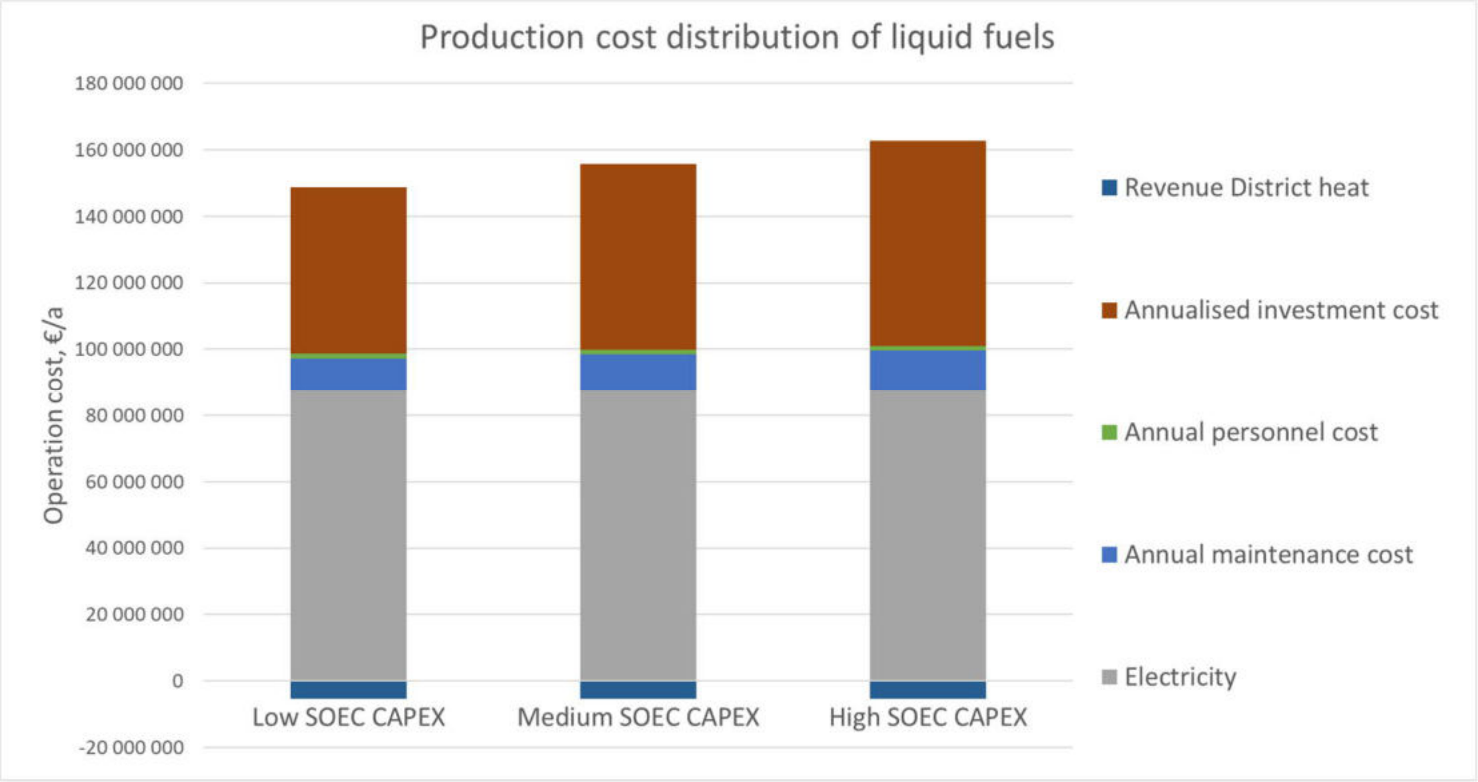
SCENARIO	BASELINE	RANGE
BY-PRODUCT PRICES		
Purge gas	0 €/MWh	
Heat	20 €/MWh	
COSTS		
Electricity prices (incl. Transmission and taxes)	35 €/MWh	20 - 50 €/MWh
Water	0.2 €/m^3	
Waste water	1.7 €/m^3	
Annual maintenance cost	2 % of the investment	
Labour cost per person for employer	60 000 €/a per person	
Labour (5 shifts)	5 person/shift	
FINANCIAL PARAMETERS		
Rate of return	8 %	
Economic lifetime of the plant	20 a	

Preliminary production cost estimation

- Production cost estimate of liquid fuels assuming electricity price 35 €/MWh
  - 1300-1400 €/t when SOEC CAPEX is 600-1000 €/kW

- Investment and electricity price are the most significant economic cost factors

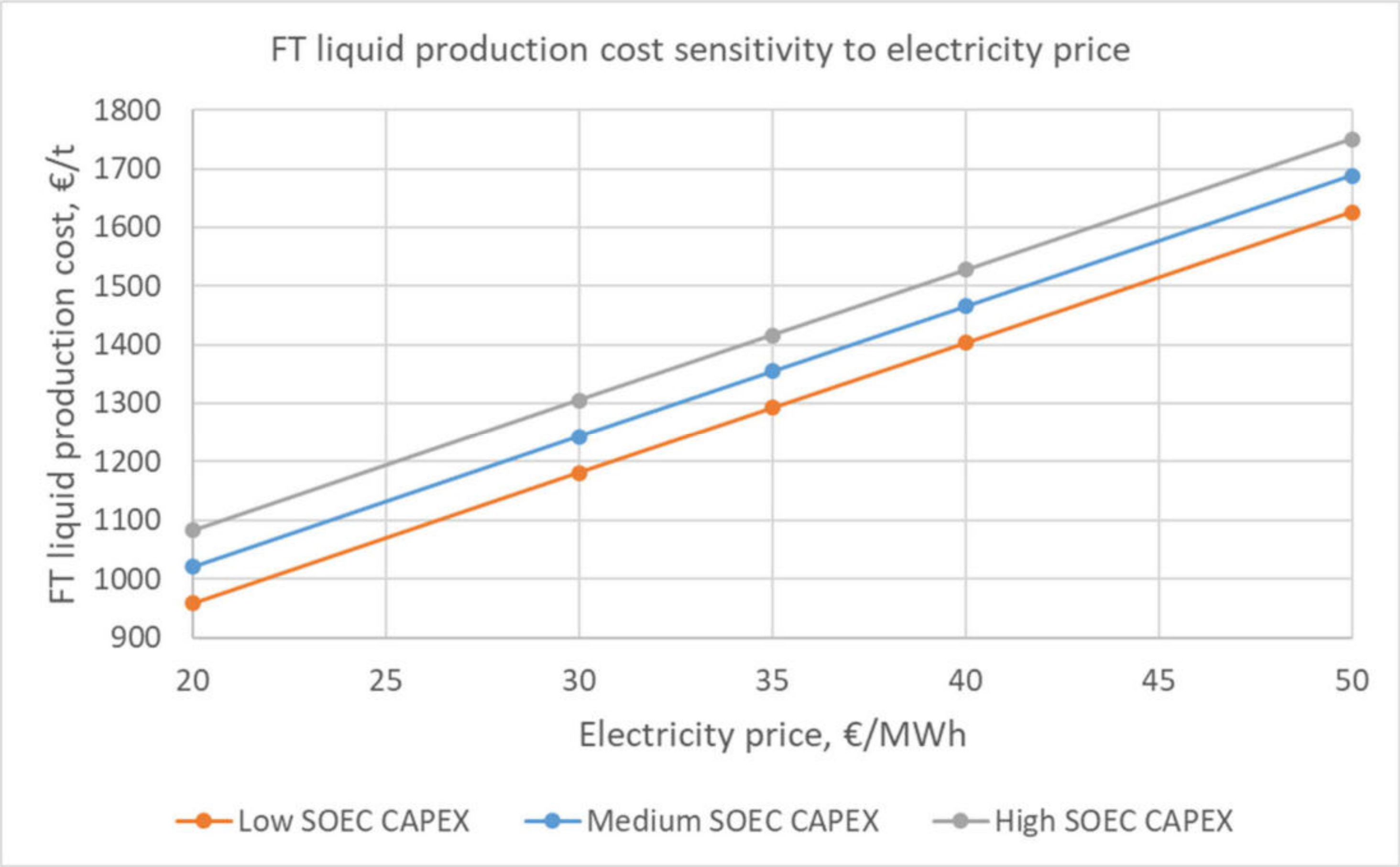
- Assumptions related to SOEC have strong effect to the economics



Preliminary sensitivity of production cost to electricity price

- Production cost of liquid fuels ranges from 1000-1700 €/t depending when electricity price range is from 20-50 €/MWh

- Electricity price has stronger effect than the SOEC price in the range of 600-1000 €/kW



Summary

- Electricity price and CAPEX estimate are the most significant cost factors
  - Assumptions related to SOEC have strong effect to the economics

- Production cost of liquid fuels ranges from 1000-1700 €/t depending when electricity price range is from 20-50 €/MWh

Uncertainties and limitations of the techno-economic assessment

- CAPEX estimate has high uncertainty
- SOEC lifetime assumed 20 years
- Continuous operation on renewble electricity
- Average revenue for heat assumed year around
- Catalyst costs not taken into account
- Refinery section model a simplified solution

beyond
the obvious

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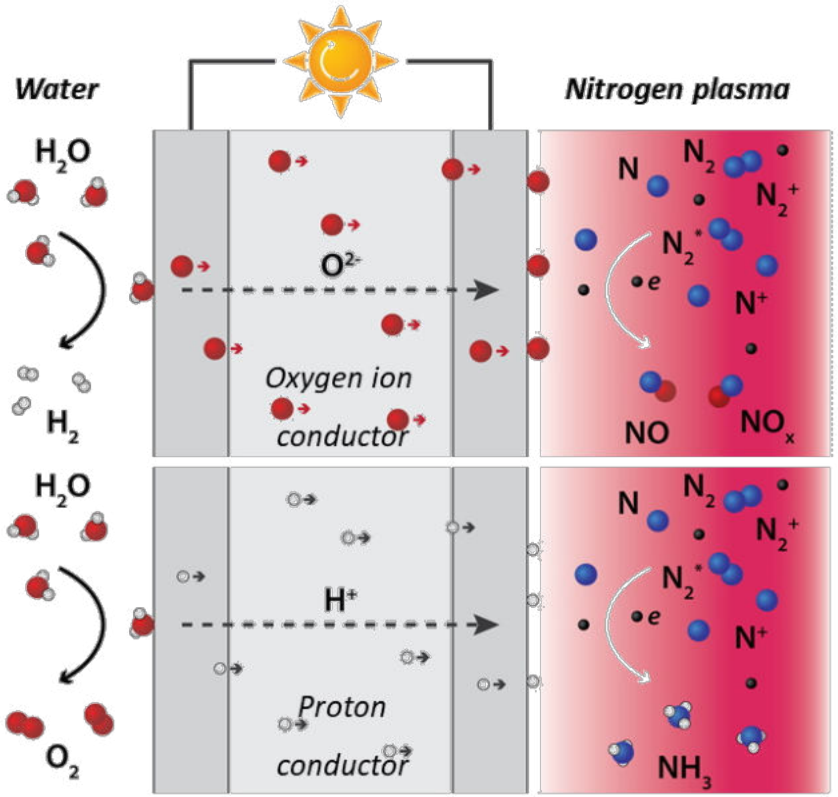
Synergistic combination of plasma activation and electrocatalysis for nitrogen fixation by water

R. Sharma, S. Welzel, M.C.M. van de Sanden,
M.N. Tsampas, Group leader

10-11 Feb 2022,
Future directions in research on Power-to-X
for sustainable chemicals & fuels



Group research in a nutshell …

DIFFER Solar fuels research focusses on novel materials, processes and

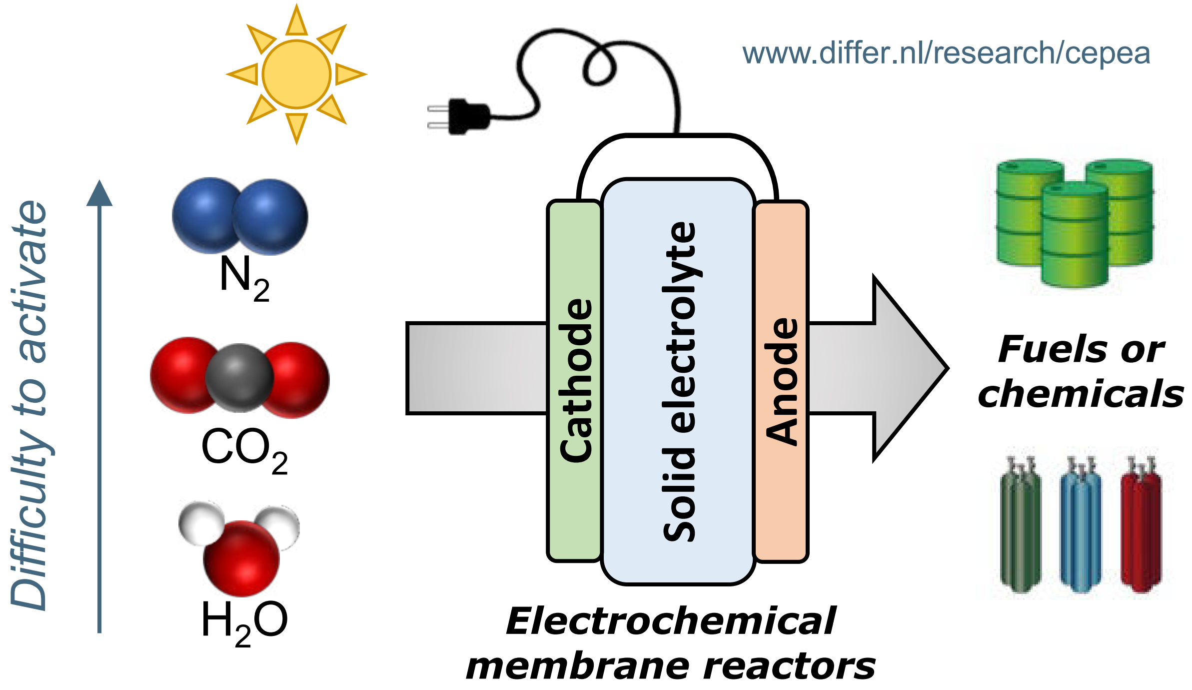
CO_2-neutral fuels and chemicals

- Seasonal and regional energy storage
- Sustainable feedstock for green industry

Activation of base molecules

- *Electrocatalysis (H_2O, CO_2)*
- *Plasma catalysis (N_2,CO_2)*

www.differ.nl/research/cepea



Difficulty to activate

N_2

CO_2

H_2O

Cathode

Solid electrolyte

Anode

Fuels or chemicals

Electrochemical membrane reactors

*We employ various types of **electrochemical membrane reactors** that allow us to couple **renewable energy-driven processes** to a wide range of applications e.g. water electrolysis, electro-fixation of nitrogen and carbon dioxide.*

The relevance of nitrogen fixation

- **Main application:** Fertilizers
- **Industrial process:** large-scale, energy-intensive
    - **CO_2 emissions:** 1% of worldwide (7% of NL)
- **World market:** 180 Mt/yr
    - Growing due to increasing food demand
- **Future potential:** energy carrier (storage and conversion)

J.W. Erisman et al, Nat. Geosci., 2008

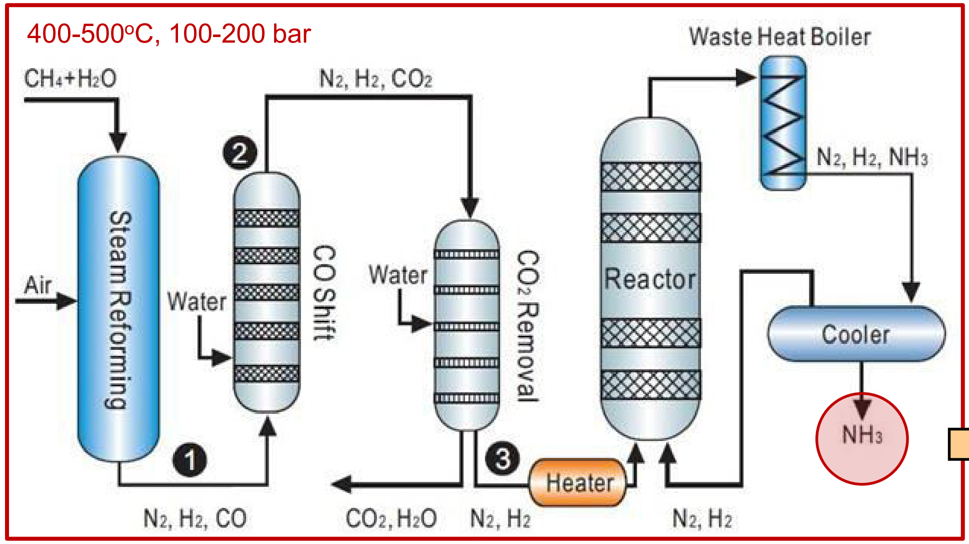
A look at the industrial approach

Industrial processes

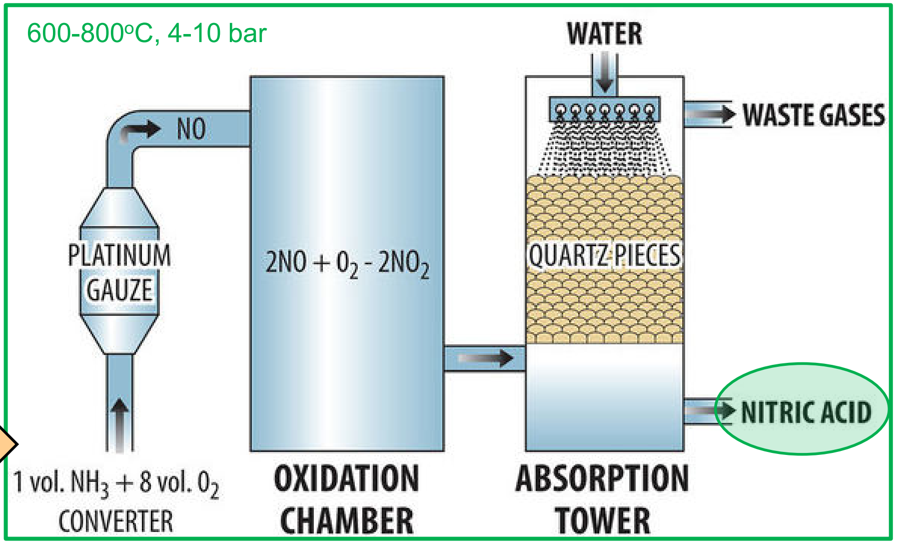
- Thermal catalysis
- Activation via high T & P
- Nitrogen fixation for fertilizers
  - Haber Bosch (*CH_4 based with high CO_2 emissions)*
  - Ostwald process *(NH_3 comes from H-B)*

CO_2 neutral nitrogen fixation

- Renewables
- Electrically driven process
  - Electrocatalysis
  - Plasma catalysis


400-500^{o}C, 100-200 bar

http://www.quantitech.co.uk/entity-287-Ammonia-Synthesis.aspx

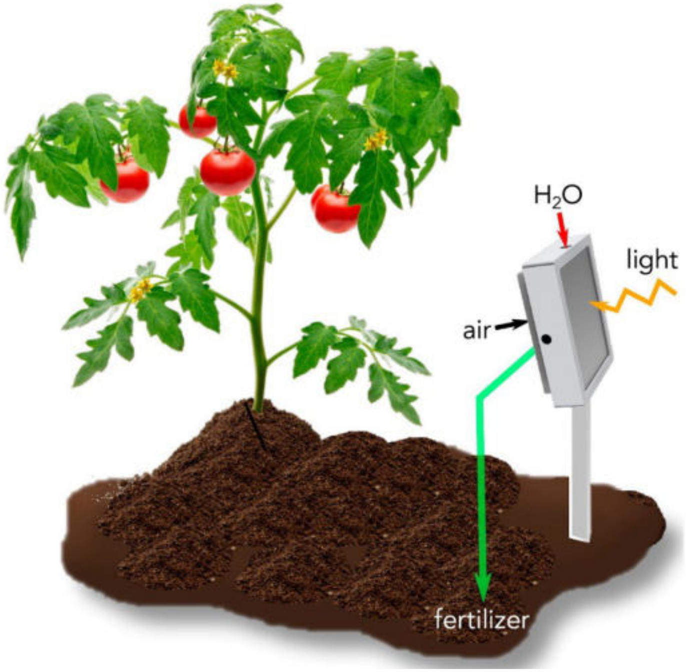

600-800^{o}C, 4-10 bar

https://ostwaldnitricoxide.weebly.com/safety-and-cost-considerations.html

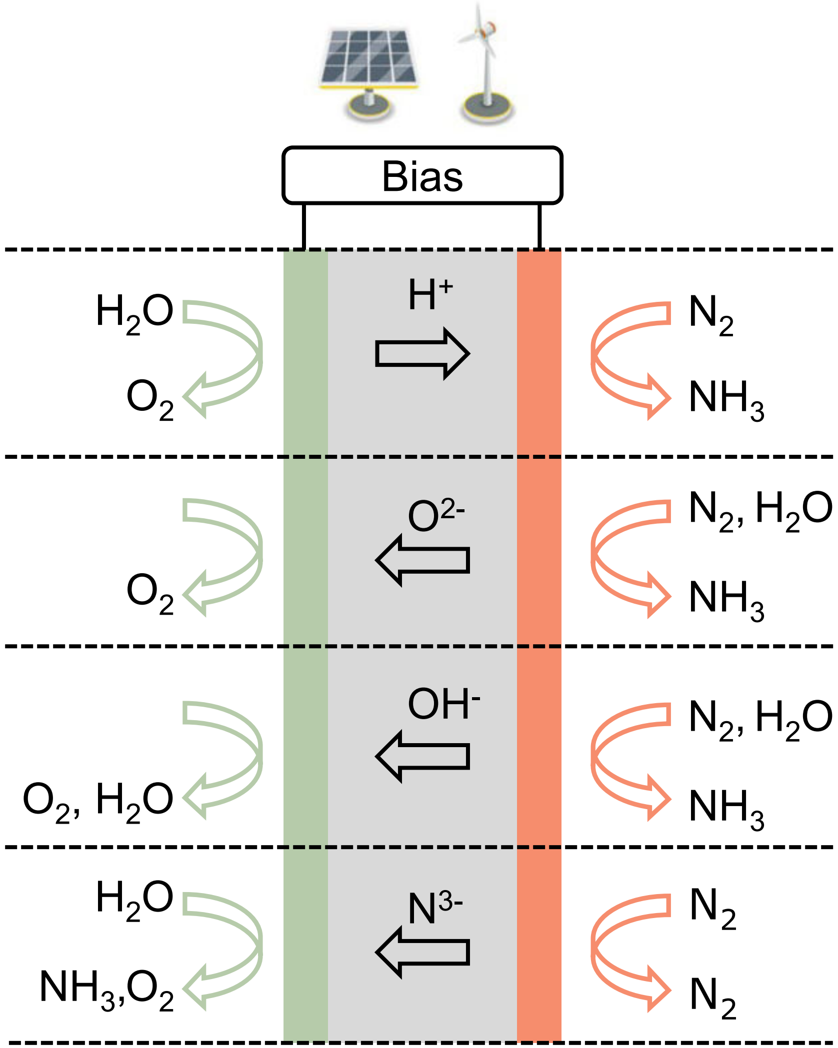
Electrocatalysis for nitrogen fixation: Ammonia

Electrocatalysis

- Green process
- Reactants: N_2 and H_2O
- Selectivity (N_2RR vs HER) and productivity issues
- Multiple approaches (ionic agents)
- Material research



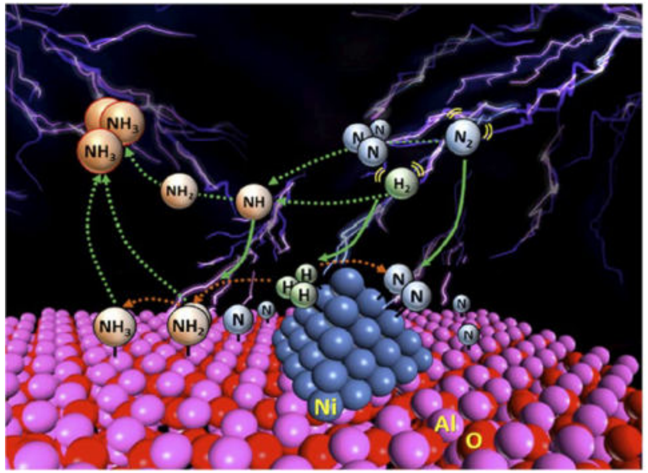
A.J.Martin et al, Chem, 2019



V. Kyriakou et al, Catal. Today, 2017

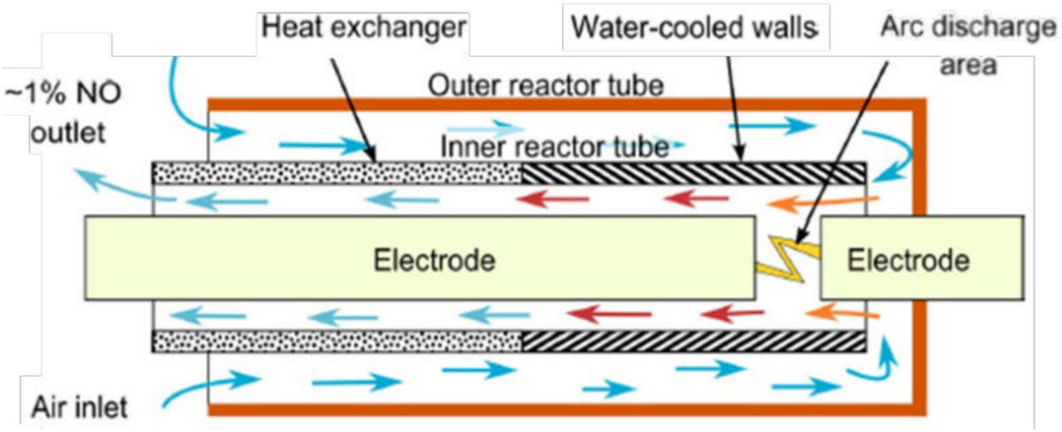
Plasma for nitrogen fixation: Ammonia and nitric oxide

A. Ammonia synthesis



Y. Wang et al, ACS Catalysis, 2019

B. Nitric oxide synthesis (Birkeland-Eyde process)

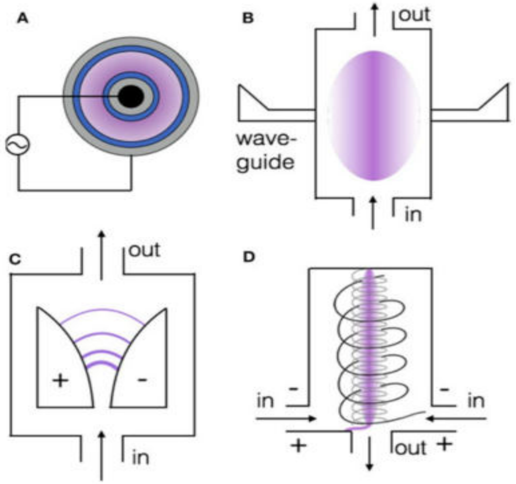


N. Cherkasov et al, Chemical Engineering and Processing, 2015

Plasma aided catalysis

- Green process
- Reactants: (a) $N_2 + H_2$* and (b) $N_2 + O_2$

  **Water electrolysis step is needed* (italic)
- Energy efficiency considerations
- Multiple approaches
- Plasma activation is not selective
  - Cofeeding of reactants is not ideal

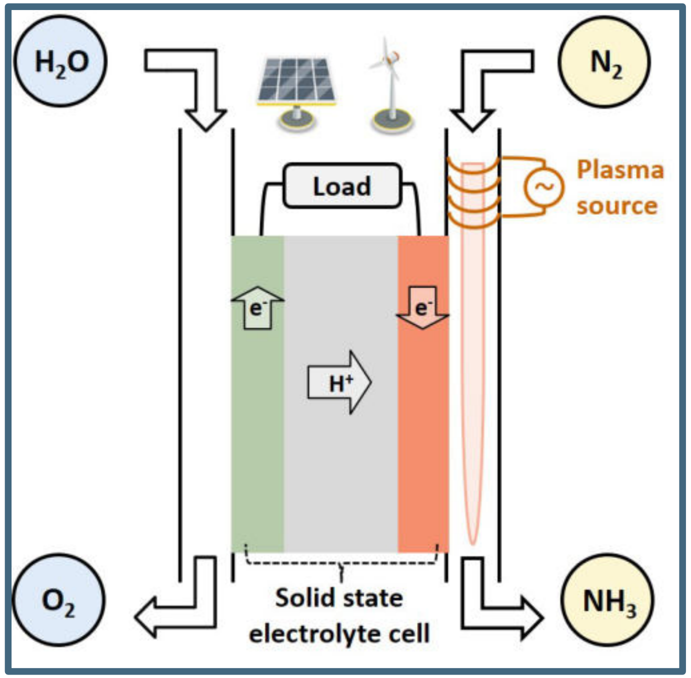


A. Bogaerts and G. Centi , Frontiers in energy research, 2020

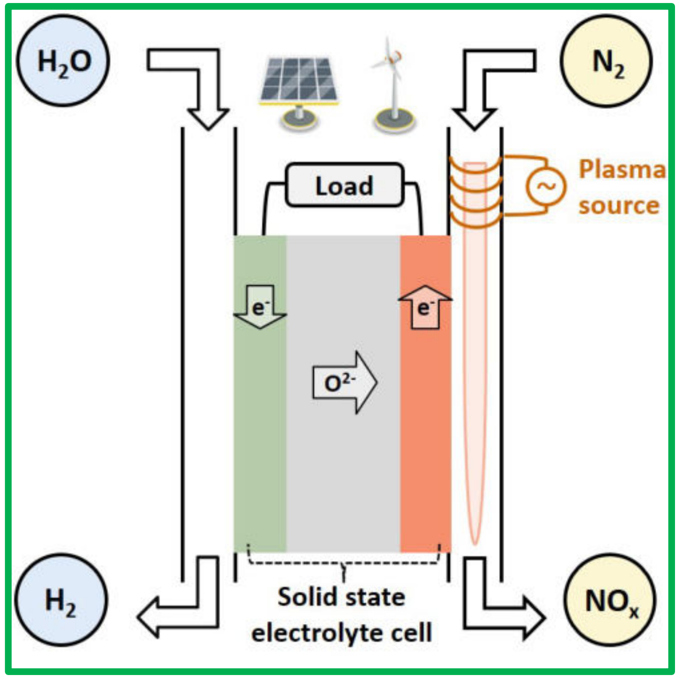
Looking for synergy: plasma + electrocatalysis

Concept

Water oxidation or **reduction** is realized in one compartment for supplying reacting species (i.e. **protons** or **oxygen ions)** via the **solid electrolyte (membrane)** to the **plasma activated nitrogen** compartment for either NH_3 or NO production.



Water compartment

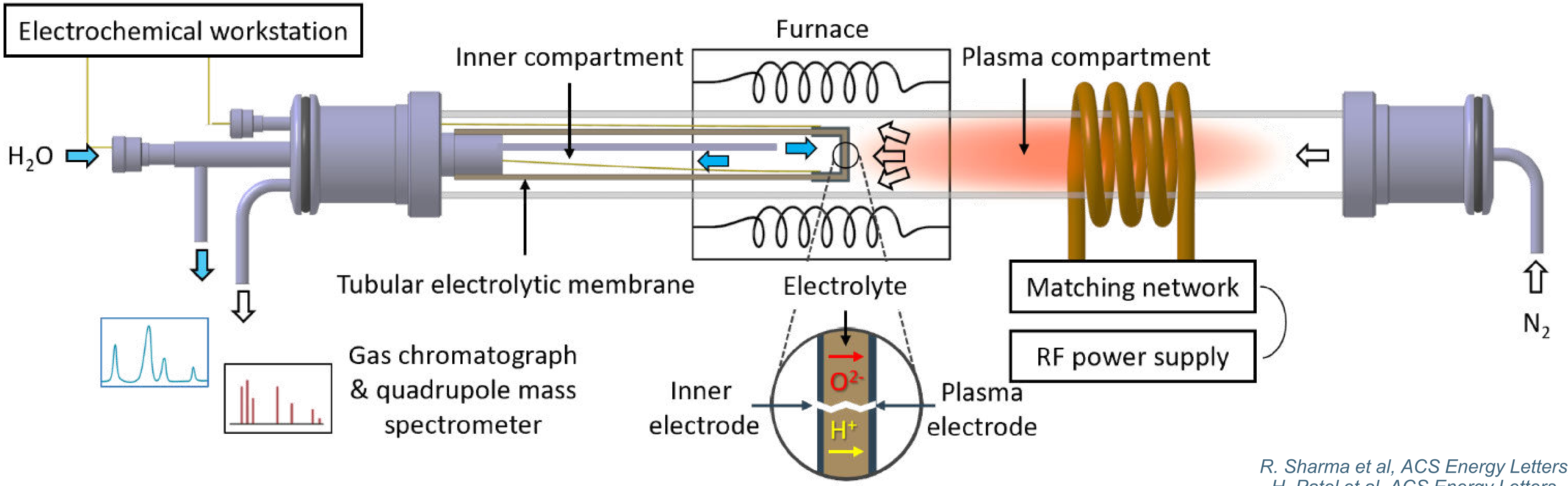


Plasma compartment

Advantages

- All electric with H_2O (or CO_2) and N_2 as feedstock
- Spatially separated reactants
  - Energy is directed to activate N_2
- Applied current controls the rate of supplied H^+ or O^{2-}
  - N_2 activation for boosting selectivity

Implementation: Reactor configuration



R. Sharma et al, ACS Energy Letters, 2021
H. Patel et al, ACS Energy Letters, 2019
Ricard et al, Curr. Appl. Phys. 2017

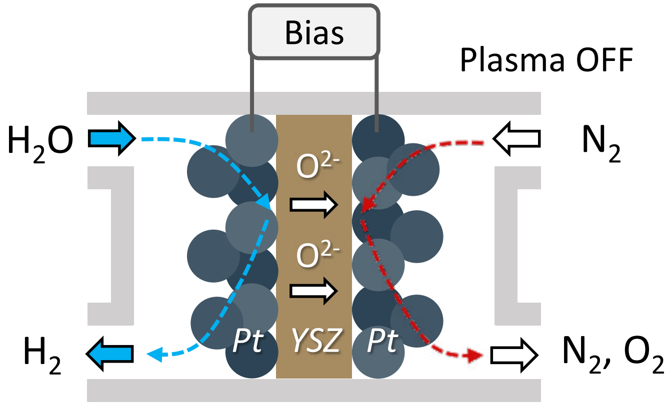
Plasma activated electrochemical membrane reactor (EMR)

- SOEC: Ceramic tubular membrane (solid electrolyte), O^{2-} or H^+ conductivity
- Dual chamber reactor: Counter electrode/Membrane/Plasma electrode (electrocatalyst)
- Low pressure (~5 mbar) RF plasma: Voluminous and well characterized
- Furnace allows operation at elevated temperature – catalysis; conductivity
- Catalyst is exposed to plasma afterglow: i.e. catalysis happens far from the plasma active zone

Nitric oxide synthesis
Proof of concept

Nitric oxide synthesis

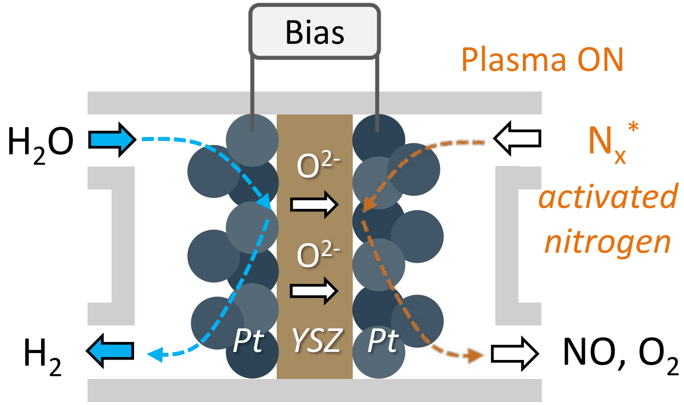
Conventional SOEC electrolysis



Cathodic half reaction:
$H_2O + 2e^- \rightarrow H_2 + O^{2-}$

Anodic half reaction:
$O^{2-} \rightarrow ½\ O_2 + 2e^-$

Plasma activated SOEC electrolysis



Cathodic half reaction:
$H_2O + 2e^- \rightarrow H_2 + O^{2-}$

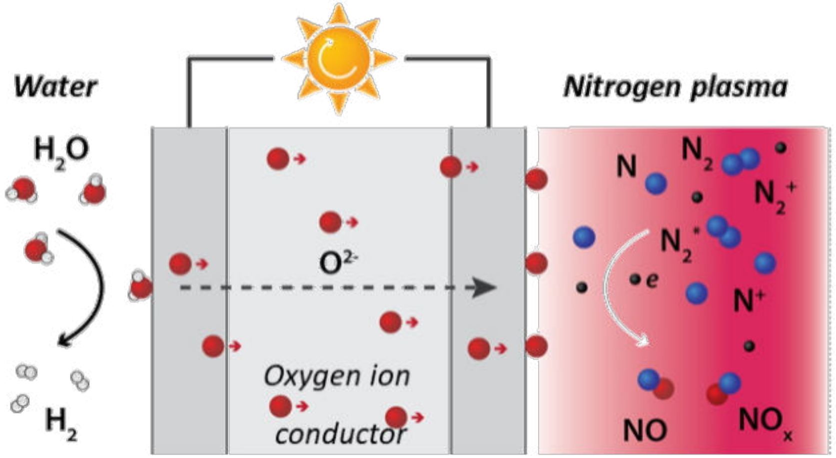
Anodic half reactions:
$O^{2-} \rightarrow ½\ O_2 + 2e^-$
$xO^{2-} + N_x^* \rightarrow xNO + 2xe^-$

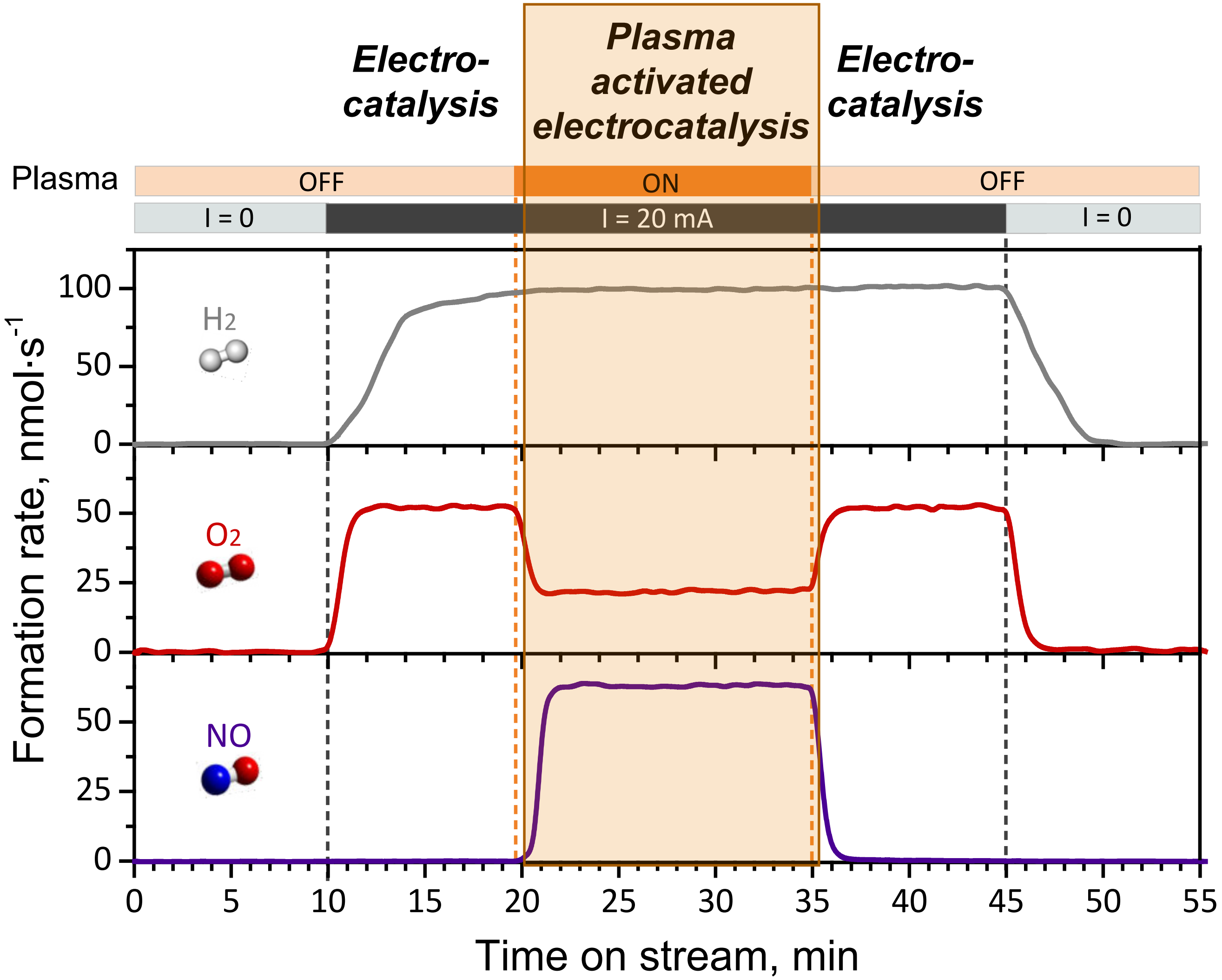
Transient experiments

- Online analysis of products
- Multiple steps

- **O^{2-} conducting EMR** and Pt electrodes.
- Two competing reactions on plasma exposed electrocatalyst
  - **O_2 evolution** and **NO_x formation.**

Nitric oxide synthesis and hydrogen cogeneration



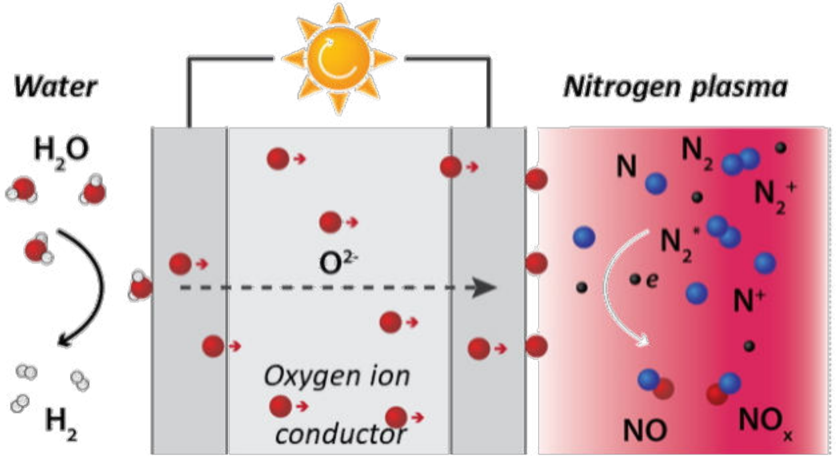


Experimental conditions

- $T=650^oC$
- N_2 - 100 cc/min
- 3.5% H_2O/He - 50cc/min
- Electrode geometrical area 20 cm^2

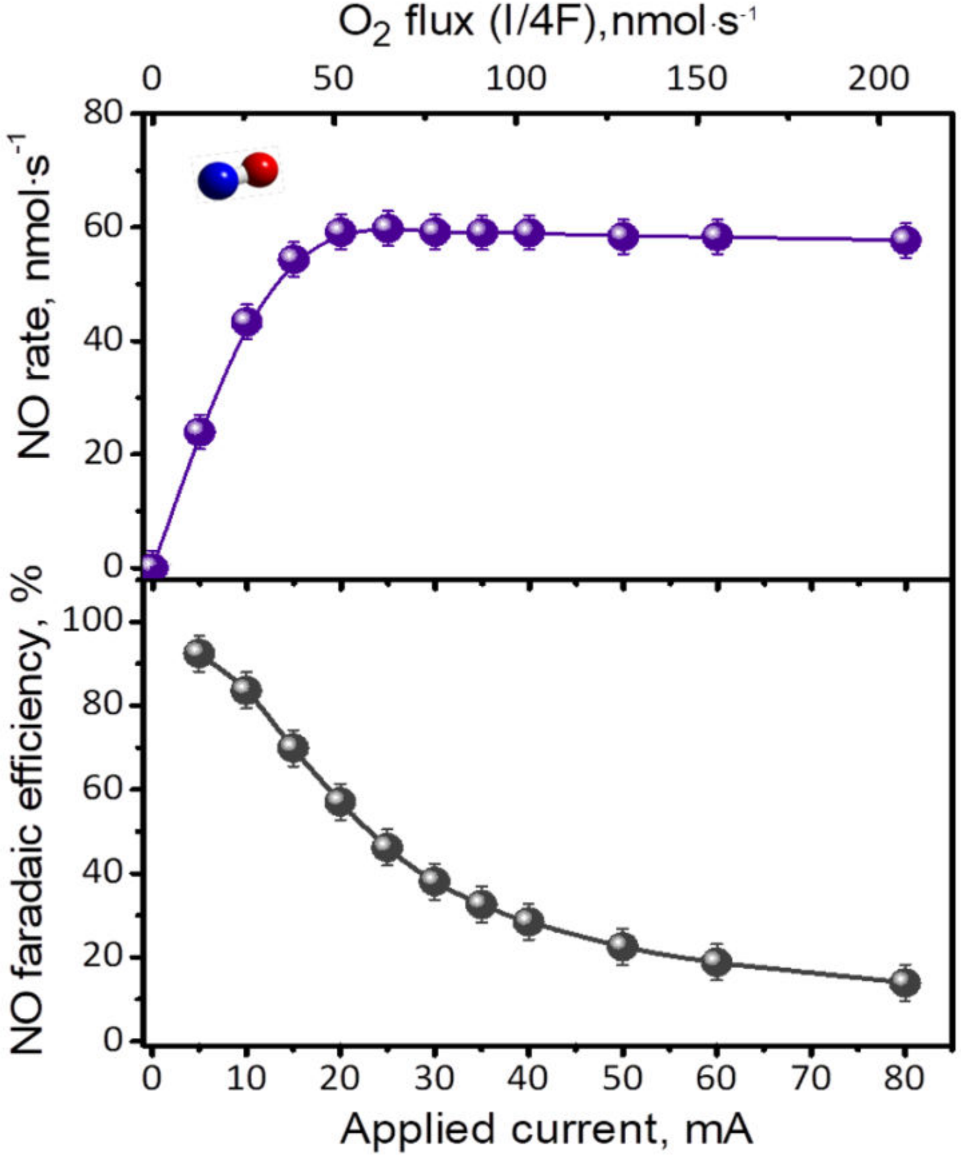
H. Patel et al, ACS Energy Letters, 2019

Effect of applied current



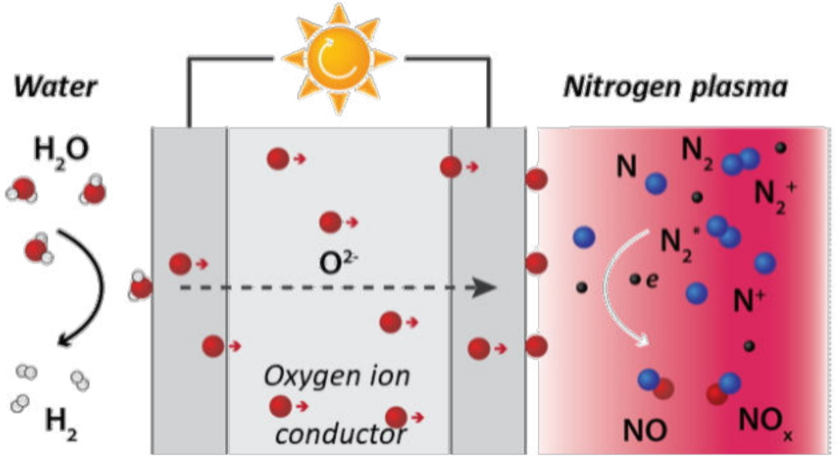
Operation and observations

- Applied current → oxygen flux
- Faradaic efficiency → selectivity to NO
- Rate vs current behavior
  - Limited supply of activated species on the catalyst active sites
  - Oxygen coverage
- NO concentration is up to 3 orders of magnitude higher than “equilibrium”

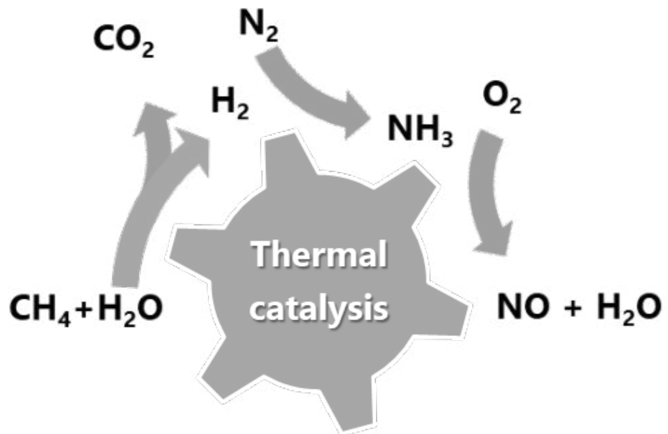


H. Patel et al, ACS Energy Letters, 2019

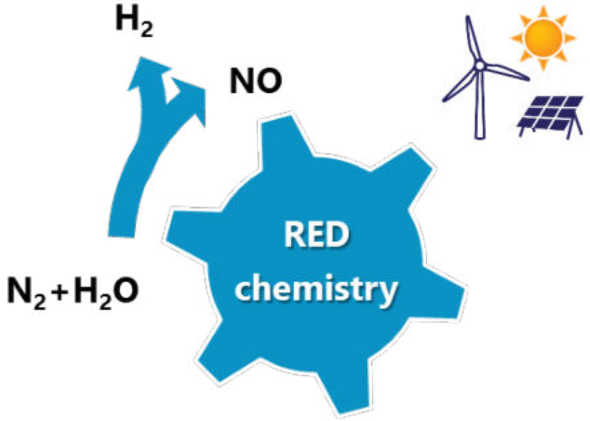
Nitric oxide synthesis and hydrogen cogeneration



Haber-Bosch and Ostwald first step



Our approach based on Renewable Energy Driven chemistry



Key findings

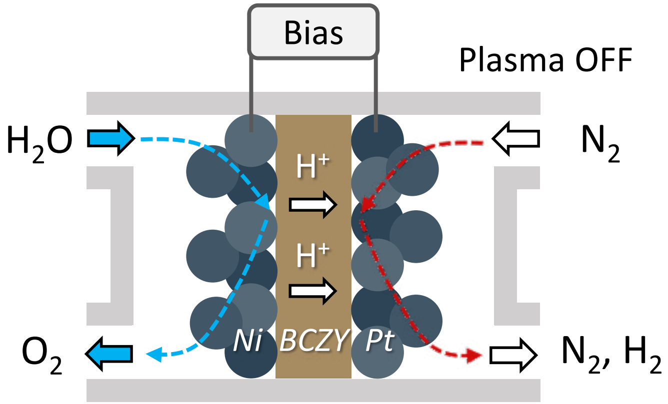
- Proof of concept
- Co-generation of H_2 and NO
- Valorization of both electrode reactions
- Further investigations are needed on
  - Selectivity
  - Productivity

H. Patel et al, ACS Energy Letters, 2019

Ammonia synthesis
Proof of concept

Ammonia synthesis

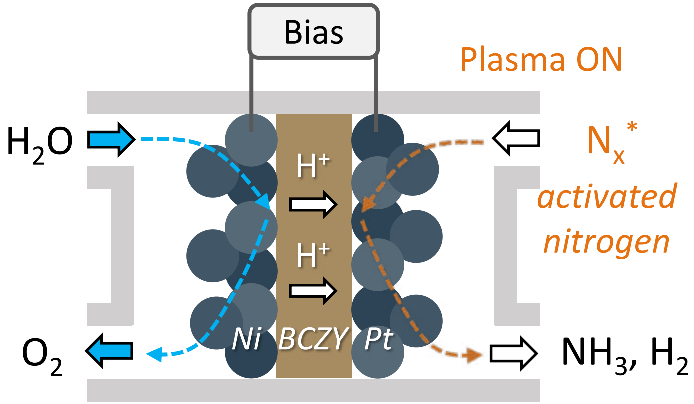
Conventional SOEC electrolysis



Anodic half reaction:
$H_2O \rightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$

Cathodic half reaction:
$2H^+ + 2e^- \rightarrow H_2$

Plasma activated SOEC electrolysis



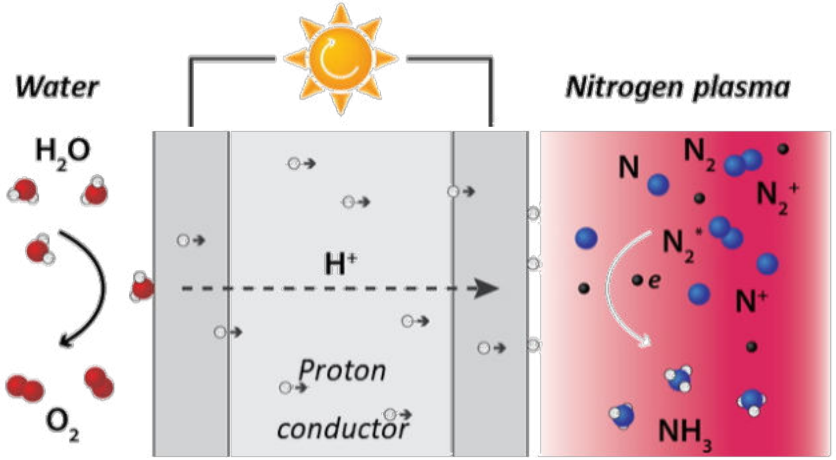
Anodic half reaction:
$H_2O \rightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$

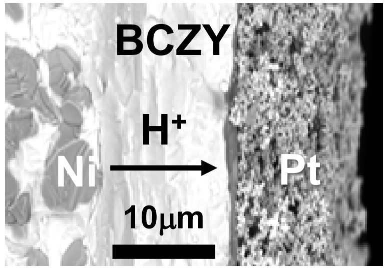
Cathodic half reaction:
$2H^+ + 2e^- \rightarrow H_2$
$3xH^+ + N_x^* \rightarrow xNH_3 + 3xe^-$

Transient experiments
- Online analysis of products
- Multiple steps

- **Proton conducting EMR** and Ni, Pt electrodes.
- Two competing reactions on plasma exposed electrocatalyst
  - **H_2 evolution** and **NH_3 formation**.

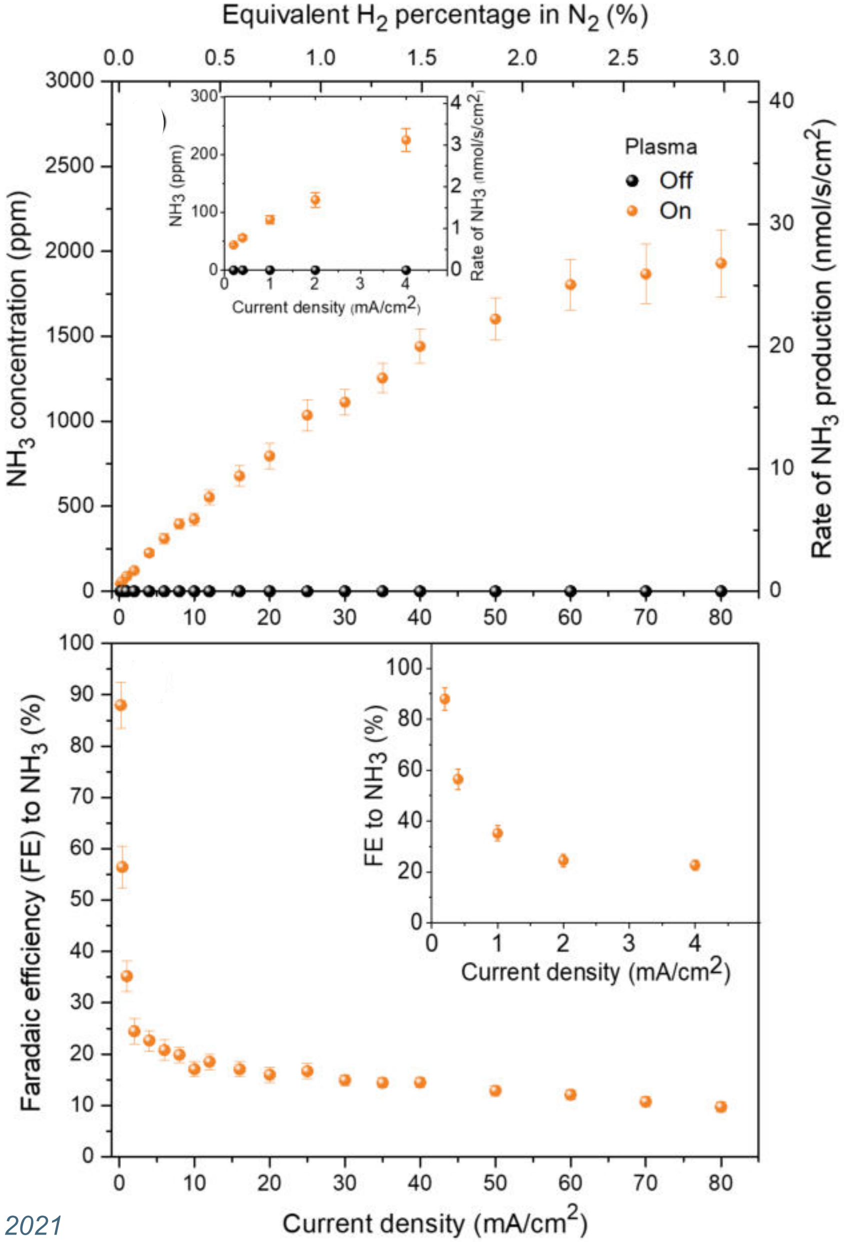
Effect of applied current





Operation and observations

- Applied current → proton flux
- Faradaic efficiency → selectivity to NH_3
- NH_3 concentration is up to 4 orders of magnitude higher than "equilibrium"

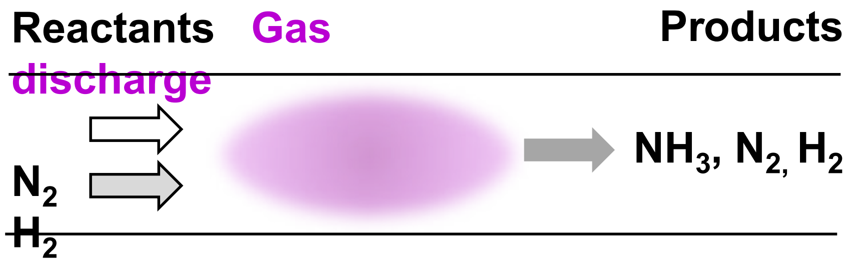


R. Sharma et al, ACS Energy Letters, 2021

Plasma operation modes

- **Pure plasma and plasma catalysis**
  - Reactants co-fed in the inlet
    - Both are activated by plasma
    - Product decomposition
    - Energy losses
- **Plasma catalysis**
    - Catalyst assist in kinetics
- **Plasma electrocatalysis**
  - Reactants are spatial separated!
  - Plasma stimulus only to desired reactant
  - Product decomposition is hindered
  - Applied current: control on the proton flux

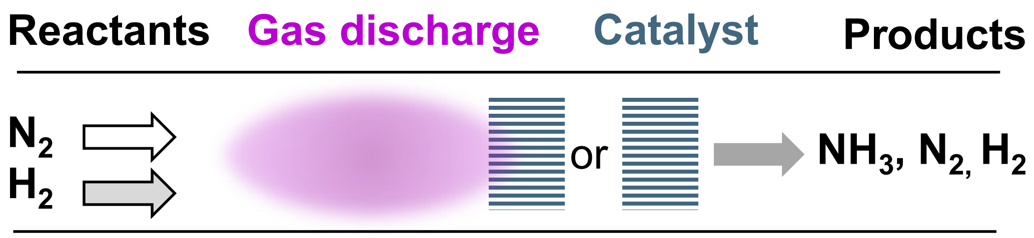
Pure plasma



Reactants **Gas discharge** **Products**

N_2 H_2 → → NH_3, N_2, H_2

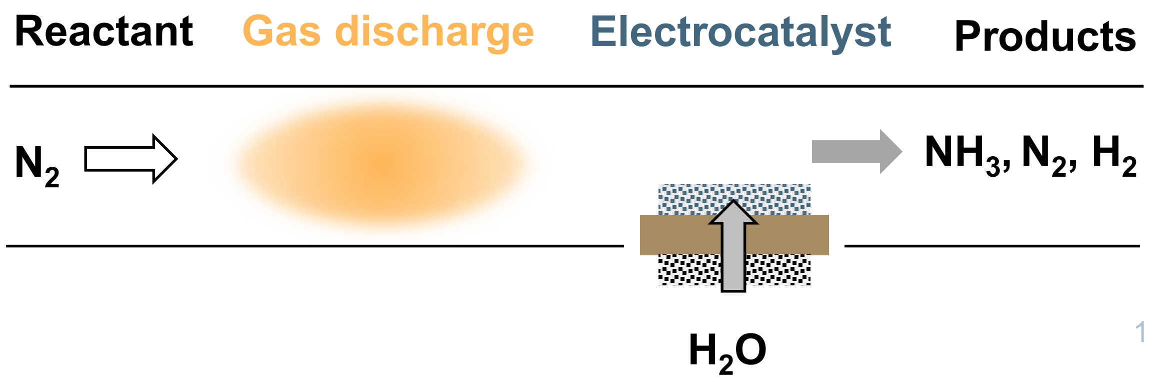
Plasma catalysis



Reactants **Gas discharge** **Catalyst** **Products**

N_2 H_2 → → or → NH_3, N_2, H_2

Plasma electrocatalysis



Reactant **Gas discharge** **Electrocatalyst** **Products**

N_2 → → NH_3, N_2, H_2

H_2O

Ammonia synthesis in three operating modes

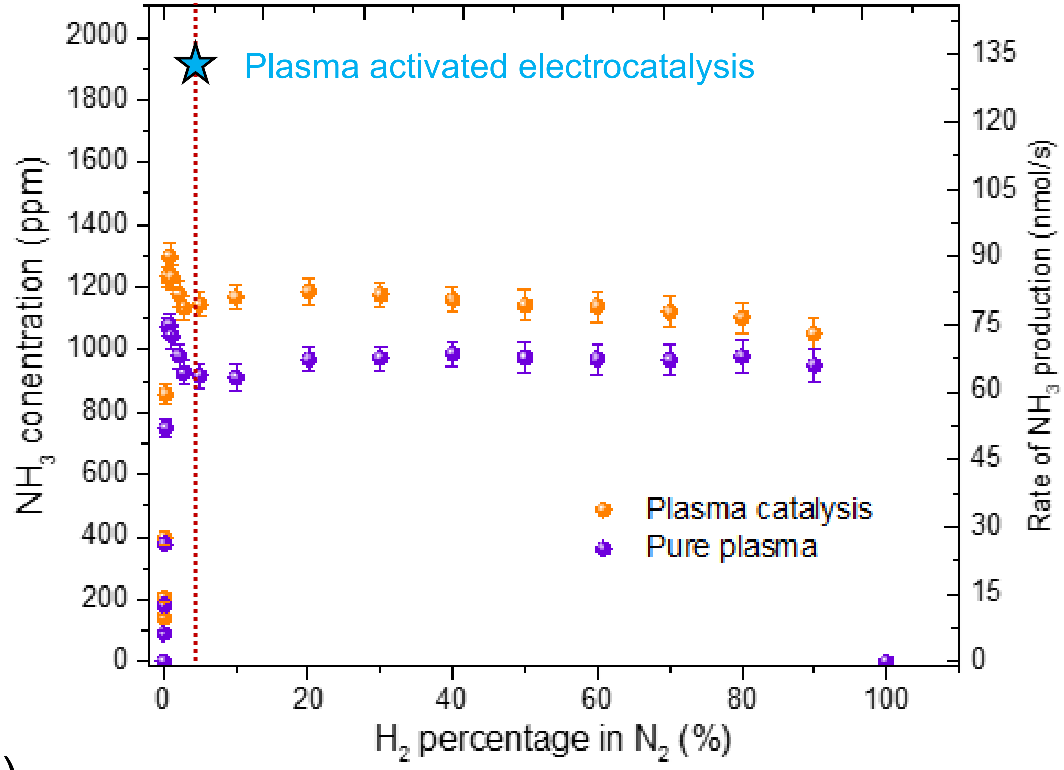
Comparison in three operation modes

- Plasma activated electrocatalysis
  - 1930 ppm NH_3
- Plasma aided catalysis
  - 1185 ppm NH_3
- Pure plasma
  - 990 ppm NH_3

Performance is influenced

- Hydrogen species adsorption pathways
  - Gas phase vs membrane
- Reactant separation
  - Product decomposition in plasma
  - Activated nitrogen densities (on catalyst) decrease due to dilution by hydrogen

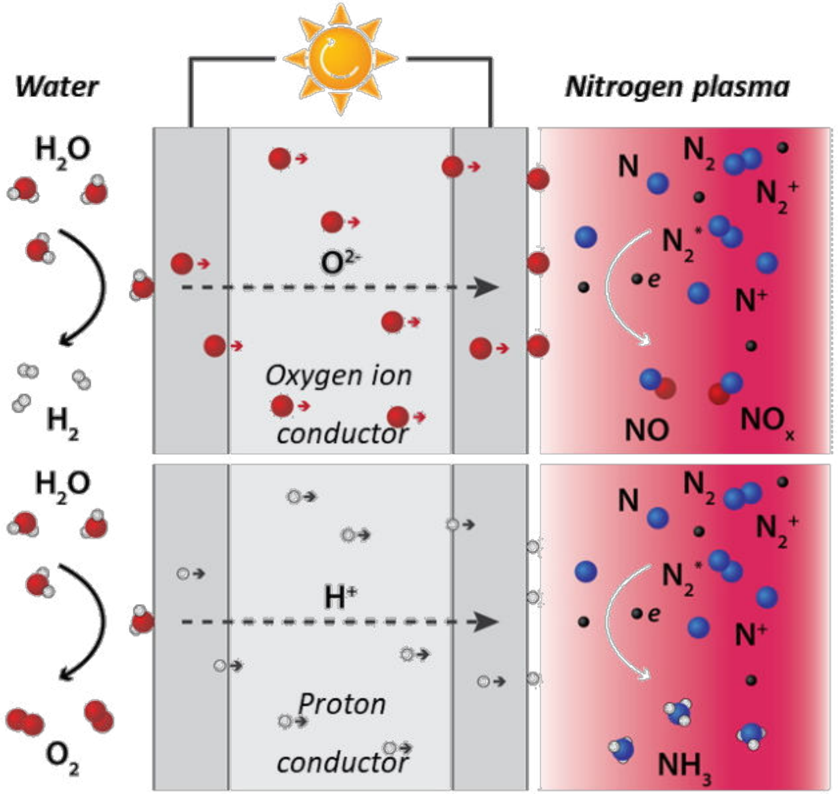
Effect of H_2/N_2 ratio in NH_3 synthesis



R. Sharma et al, ACS Energy Letters, 2021

Summary and future outlook

Summary



H. Patel et al, ACS Energy Letters, 2019
R. Sharma et al, ACS Energy Letters, 2021

<u>Key performance indicators</u>

Nitric oxide synthesis

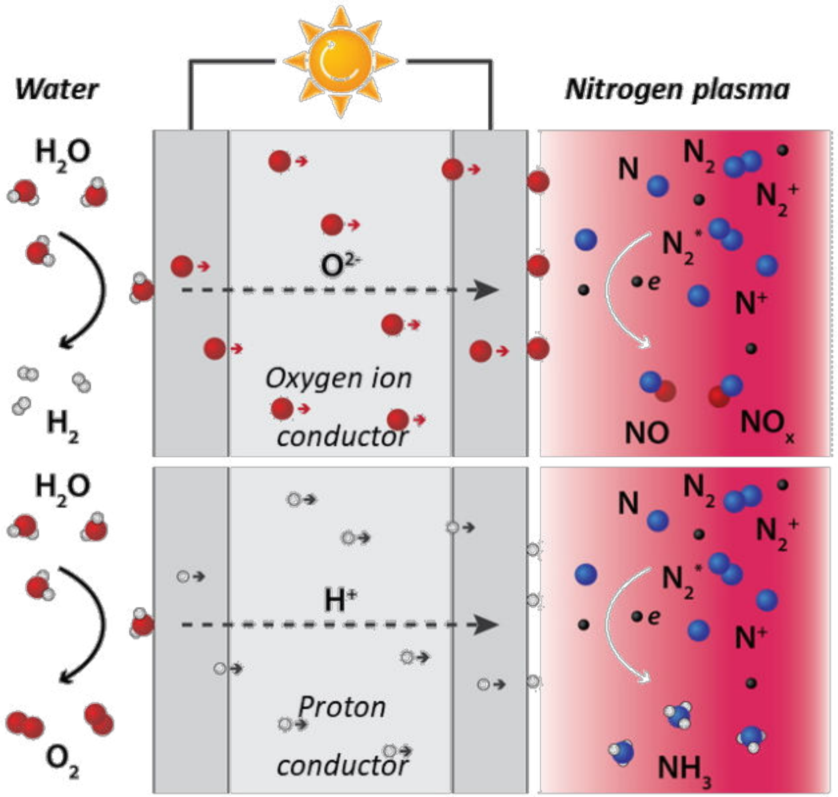
- *Up to 93% Faradaic efficiency to NO*
- *Maximum rate 3.15 nmol NO per s per cm^2*
- *NO concentration > 10^3 times equilibrium*
- *1350 MJ/N-mol (Literature: 47-2698 MJ/N-mol)*

Ammonia synthesis

- *Up to 88% Faradaic efficiency to NH_3*
- *Maximum rate 26.8 nmol NH_3 per s per cm^2*
- *NH_3 concentration > 10^4 times equilibrium*
- *605 MJ/N-mol (Literature: 47-2698 MJ/N-mol)*

- *TOF ~2.6 s^{-1} vs ~ 0.1 s^{-1} of HB*
- *<u>Plasma electrocatalysis > Plasma catalysis > Pure plasma</u>*

Future outlook



H. Patel et al, ACS Energy Letters, 2019
R. Sharma et al, ACS Energy Letters, 2021

Main strategies to optimize productivity & efficiency

- Microkinetic modeling
- Plasma characterization
- Efficient coupling of plasma flux with active catalyst sites
    - *Reactor design*
    - *Tuning plasma parameters*
    - *Advanced SOEC architectures*
    - *Electrocatalyst design*

UNIVERSITY OF NOTRE DAME

H. Ma et al, Nature Communications, 2022

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https://oracle-jp.eu/

Thank you for your attention!