International Workshop on CO_2 Capture and Utilization

TU/e - Eindhoven - 16-17 February 2021

Organized by

C4U · CONVERGE · C2FUEL · TU/e Eindhoven University of Technology

CARMOF · REALISE CCUS · eCOCO2 · MEMBER

CO2MOS · CO2FOKUS Advancing CO2 Conversion · KEROGREEN · BioCoMem

Sponsored by

NWO · processes

The projects sponsoring this workshop received support from the European Union's Horizon 2020 research and innovation under grants agreement reported below

Nº	Acronym	Project Title	Website	Grant agreement
1	MEMBER	Advanced MEMBranes and membrane assisted procEsses for pre- and post-combustion CO2 captuRe	https://member-co2.com/	760944
2	CARMOF	TAILOR-MADE 3D PRINTED STRUCTURES BASED ON CNTS AND MOFS MATERIALS FOR EFFICIENT CO2 CAPTURE	https://carmof.eu/	760884
3	BIOCOMEM	Bio-based copolymers for membrane end products for gas separations	https://www.biocomem.eu/	887075
4	C2FUEL	Carbon Captured Fuel and Energy Carriers for an Intensified Steel Off-Gases based Electricity Generation in a Smarter Industrial Ecosystem	https://c2fuel-project.eu/	838014
5	COZMOS	Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS	https://www.spire2030.eu/cozmos	837733
6	eCOCO2	Direct electrocatalytic conversion of CO2 into chemical energy carriers in a co-ionic membrane reactor	https://ecocoo.eu/	838077
7	CO2Fokus	CO2 utilisation focused on market relevant dimethyl ether production, via 3D printed reactor- and solid oxide cell-based technologies	https://www.co2fokus.eu/	838061
8	C4U	Advanced Carbon Capture for steel industries integrated in CCUS Clusters	https://c4u-project.eu/	884418
9	REALISE	Demonstrating a Refinery-Adapted Cluster-Integrated Strategy to Enable Full-Chain CCUS Implementation	https://realiseccus.eu/	884266
10	CONVERGE	CarbON Valorisation in Energy-efficient Green fuels	https://www.converge-h2020.eu/	818135
11	KEROGREEN	Production of Sustainable aircraft grade Kerosene from water and air powered by Renewable Electricity, through the splitting of CO2, syngas formation and Fischer-Tropsch synthesi	http://www.kerogreen.eu/	763909

Carbon-intensive industries are mandatory to supply processed materials and products to cover EU citizen's needs. In a vision of a decarbonized Europe, these industries are always seen as negative components due to their massive CO_2 emissions but also since only 14% of the energy used to run these factories is coming from renewable sources.

What if we were able to generate additional value, capturing CO_2 flue gases & convert it into a fuel and energy carrier that could be used locally?

There is a large consensus at European level that CO_2 capture, either from energy intensive industries or even from air, is a necessity to be able to reduce the human effect on the observed climate changes.

At the same time, CO_2 is increasingly seen as a potential raw material for the C1 chemistry or to be used as energy carrier.

Several projects are running in parallel at national and international levels. This workshop gathered the last scientific results of the different running projects and made them available for scientists and students and industrial researchers in an informal atmosphere.

The scientific goal was to create a forum for open discussion on the latest developments on technologies for CO_2 capture and conversion. We think that the workshop should be open to all, without registration fees, and as such several projects decided to try to (partially) cover the costs of the workshop. In this way, also young students could participate freely and have the possibility to discuss the topic and the last developments in the field.

Chairman

Prof. Fausto Gallucci – Eindhoven University of Technology

Local organizing Committee

Fausto Gallucci
Fernanda Neira D’Angelo
Aitor Cruellas
Camilla Brencio
Brandon Leal
Sirui Li
Arash Rahimali
Berenger Wegman
Saskia Walravens

Program

Day 1

	Opening & Plenary sessions (chairperson Fausto Gallucci)	
9:00-9:30	All coordinators - Introduction to projects	
9:30-10:00	Dr. E. De Coninck (CTO ArcelorMittal) - The zero Emission Plant	
10:00-10:30	Dr. Walter Eevers (CO2 Value Europe)	
10:30-11:15	Coffee break and posters	
	Session 1A (chairperson Jose Luis Viviente)	***Session 1B (chairperson Camel Makhloufi)***
11:15-11:35	Dr. O. David - A review of the membrane development steps from material to final product	Dr. M. Noponen and Dr. X. Sun - High temperature electrolysis and co-electrolysis
11:35-11:55	Dr. V. Spallina - System simulation for integration of CO_2 capture technologies into steelworks and CCUS clusters	Prof. J Serra - Direct electrocatalytic conversion of CO_2 into chemical energy carriers in a co-ionic membrane reactor
11:55-12:15	Dr. M. Saric - Methanol membrane reactor: modelling and experimental results	Dr. V. Middelkoop - CO2Fokus at a glance: CO_2 utilisation focused on DME production, via 3D printed reactor and solid oxide cell based technologies
12:15-12:35	Dr. Adam Deacon - Realising the potential of MOFs through efficient scale-up	Dr. M. Tsampas - The KEROGREEN CO_2 plasma route to CO and alternative fuels
12:35-12:55	Dr. M. Etxeberria-Benavides - PBI based mixed matrix hollow fiber membranes for pre-combustion CO_2 capture	Dr. G. Bonura - 3D-printing in catalysis: Development of efficient hybrid systems for the direct hydrogenation of CO_2 to DME
12:55-14:00	Lunch break	
	Plenary session (chairperson Fausto Gallucci)	
14:00-15:00	Dr. Angels Orduna (Spire 2030)	
	Session 2A (chairperson Giampaolo Manzolini)	***Session 2B (chairperson Vesna Middelkoop)***
15:00-15:20	Dr. G. Garcia - LCA and TEA of the COZMOS technology	Dr. M. Sleczkowski and Dr. Pablo Ortiz - Turning gas separation membranes green with biobased block copolymers
15:20-15:40	Dr. A. Mattos or Dr. A. Mitchell - How can public policy and business model innovation be developed to address challenges of CCUS and realise the opportunity?	Dr. A. Benedito - CARMOF Project: a CO_2 capture demonstrator based on membrane and solid sorbents hybrid process
15:40-16:00	Dr. L. Engelmann - Perception of CO_2-based fuels and their production in international comparison	Dr. R.H. Heyn - Introduction to the COZMOS project
16:00-16:20	Dr. N. Dunphy - Social studies in REALISE project	Dr. L. Petrescu - Converge technology for efficiency methanol production with negative CO_2 emissions: energy and environmental analysis
16:20-17:05	Coffee break and posters	

Day 2

	Opening & Plenary Sessions (chairperson Fernanda Neira D'Angelo)	
9:30-10:00	All coordinators - Introduction to projects	
10:00-11:00	Dr. K. Bakke - Northern Lights – concept, plans and future	
11:00-11:45	Coffee break and posters	
	Session 3A (chairperson José Serra)	***Session 3B (chairperson Oana David)***
11:45-12:05	Dr. A. De Paula Oliveira - SER and SEWGS for CO_2 capture: experimental results	Msc. A. Sliousaregko - Industrial membrane requirements for CO_2 removal from different gas mixtures - Current practices and developments
12:05-12:25	MSc. S. Poto - Membrane reactors for DME production	Dr. I. Kim - Technologies demonstration in REALISE
12:25-12:45	Dr. U. Olsbye - Catalyst development within the COZMOS project	Dr. N. Kanellopoulos - Hybrid VTSA pilot plant and design of industrial demo plant for CO_2 capture
12:45-13:05	Dr. S. Krishnamurthy - CO_2 capture using 3D printed PEI adsorbents supported by carbon nanostructures	Mr. Paul Cobden and Prof. C. Abanades - Pilot preparation for demonstration in the C4U project
13:05-13:25	Dr. S. Perez - Process intensification in the conversion of CO_2 with a milli-structured reactor	Mr. T. Swinkels - Decentralized FA based power generators
13:25-13:45	Dr. F. de Sales Vidal Vazquez - The KEROGREEN syngas route to alternative fuels and chemicals	Dr. L. Roses - Design and development of a membranebased post-combustion CO_2 capture system
13:45-14:30	Lunch break	
14:30-15:30	***Round table and questions - closure (chairpersons Fausto Gallucci and Fernanda Neira)***	

Opening & Plenary sessions (chairperson Fausto Gallucci)

All coordinators - Introduction to projects

Dr. E. De Coninck (CTO ArcelorMittal) - The zero Emission Plant

Introduction to the Projects

International Workshop on CO_2 Capture and Utilization,
16-17 February 2021, TU/E, Eindhoven, The Netherlands

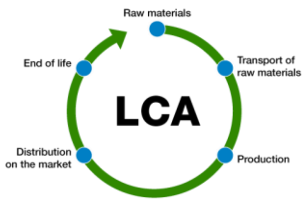
Outline

1. MEMBER
2. CARMOF
3. BIOCOMEM
4. C2FUEL
5. COZMOS
6. eCOCO2
7. CO2Fokus
8. C4U
9. REALISE
10. CONVERGE
11. KEROGREEN

№	Topic	Acronym	Project Tytle	website	Coordinator or speaker
1	NMBP-20-2017: High-performance materials for optimizing carbon dioxide capture	MEMBER	Advanced MEMBranes and membrane assisted procEsses for pre- and post- combustion CO2 captuRe	https://member-co2.com/	José Luis Viviente
2	NMBP-20-2017: High-performance materials for optimizing carbon dioxide capture	CARMOF	TAILOR-MADE 3D PRINTED STRUCTURES BASED ON CNTS AND MOFS MATERIALS FOR EFFICIENT CO2 CAPTURE	https://carmof.eu/	Adolfo Benedito
3	BBI-2019-SO3-R10 - Develop bio-based high-performance materials for various and demanding applications	BIOCOMEM	Bio-based copolymers for membrane end products for gas separations	https://www.biocomem.eu/	Oana David
4	CE-SC3-NZE-2-2018: Conversion of captured CO2	C2FUEL	Carbon Captured Fuel and Energy Carriers for an Intensified Steel Off-Gases based Electricity Generation in a Smarter Industrial Ecosystem	https://c2fuel-project.eu/	Camel Makhloufi
5	CE-SC3-NZE-2-2018: Conversion of captured CO2	COZMOS	Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS	https://www.spire2030.eu/cozmos	Richard H. Heyn
6	CE-SC3-NZE-2-2018: Conversion of captured CO2	eCOCO2	Direct electrocatalytic conversion of CO2 into chemical energy carriers in a co-ionic membrane reactor	https://ecocoo.eu/	José M. Serra
7	CE-SC3-NZE-2-2018: Conversion of captured CO2	CO2Fokus	CO2 utilisation focused on market relevant dimethyl ether production, via 3D printed reactor- and solid oxide cell-based technologies	https://www.co2fokus.eu/	Vesna Middelkoop
8	LC-SC3-NZE-5-2019-2020 - Low carbon industrial production using CCUS	C4U	Advanced Carbon Capture for steel industries integrated in CCUS Clusters	https://c4u-project.eu/	Haroun Mahgerefteh
9	LC-SC3-NZE-5-2019-2020 - Low carbon industrial production using CCUS	REALISE	Demonstrating a Refinery-Adapted Cluster-Integrated Strategy to Enable Full-Chain CCUS Implementation	https://realiseccus.eu/	Inna Kim
10	LC-SC3-RES-21-2018 - Development of next generation biofuels and alternative renewable fuel technologies for road transport	CONVERGE	CarbON Valorisation in Energy-efficient Green fuels	https://www.converge-h2020.eu/	Giampaolo Manzolini
11	LCE-06-2017 - New knowledge and technologies	KEROGREEN	Production of Sustainable aircraft grade Kerosene from water and air powered by Renewable Electricity, through the splitting of CO2, syngas formation and Fischer-Tropsch synthesi	http://www.kerogreen.eu/	Michael Tsampas

Advanced MEMBranes and membrane assisted procEsses for pre- and post- combustion CO_2 captuRe

MEMBER project aims to reduce the cost of the Carbon Dioxide capture technologies by scaling-up and manufacturing advance materials (membranes, catalysts and sorbents) to develop membrane-based technologies that outperform current technology for pre- and post-combustion CO_2 capture in power plants as well as H_2 generation with integrated CO_2 capture.



Material Production and Scale up

- Raw Material
- Processing & Scale Up

MOFs

Polymers

Mixed Matrix Hollow Fibers

Sorbents

Catalyst

Membranes

Prototype Manufacturing

- Module / Reactor
- CO_2 Capture System

Demonstration TRL 6

- Application

Pre- & Post- combustion CO_2 capture in power plants

Membrane Assisted Sorption Enhanced Reforming (MA-SER): H_2 production with integrated CO_2 capture

Performance Targets

CO_2 capture > 90%

CO_2 capture cost:
< 30 €/ton pre-
< 40 €/ton post-

CO_2 capture > 90%

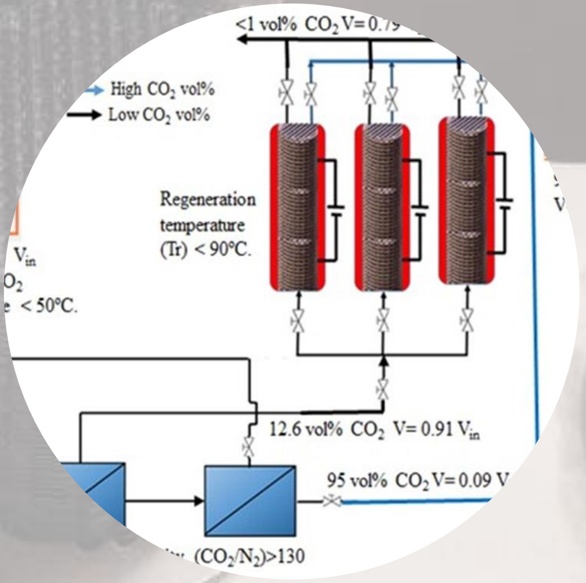
CO_2 capture cost:
< 30 €/ton pre-

https://member-co2.com/

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760944.

CARMOF Project

TAILOR-MADE 3D PRINTED STRUCTURES BASED ON CNT AND MOF MATERIALS FOR EFFICIENT CO2 CAPTURE

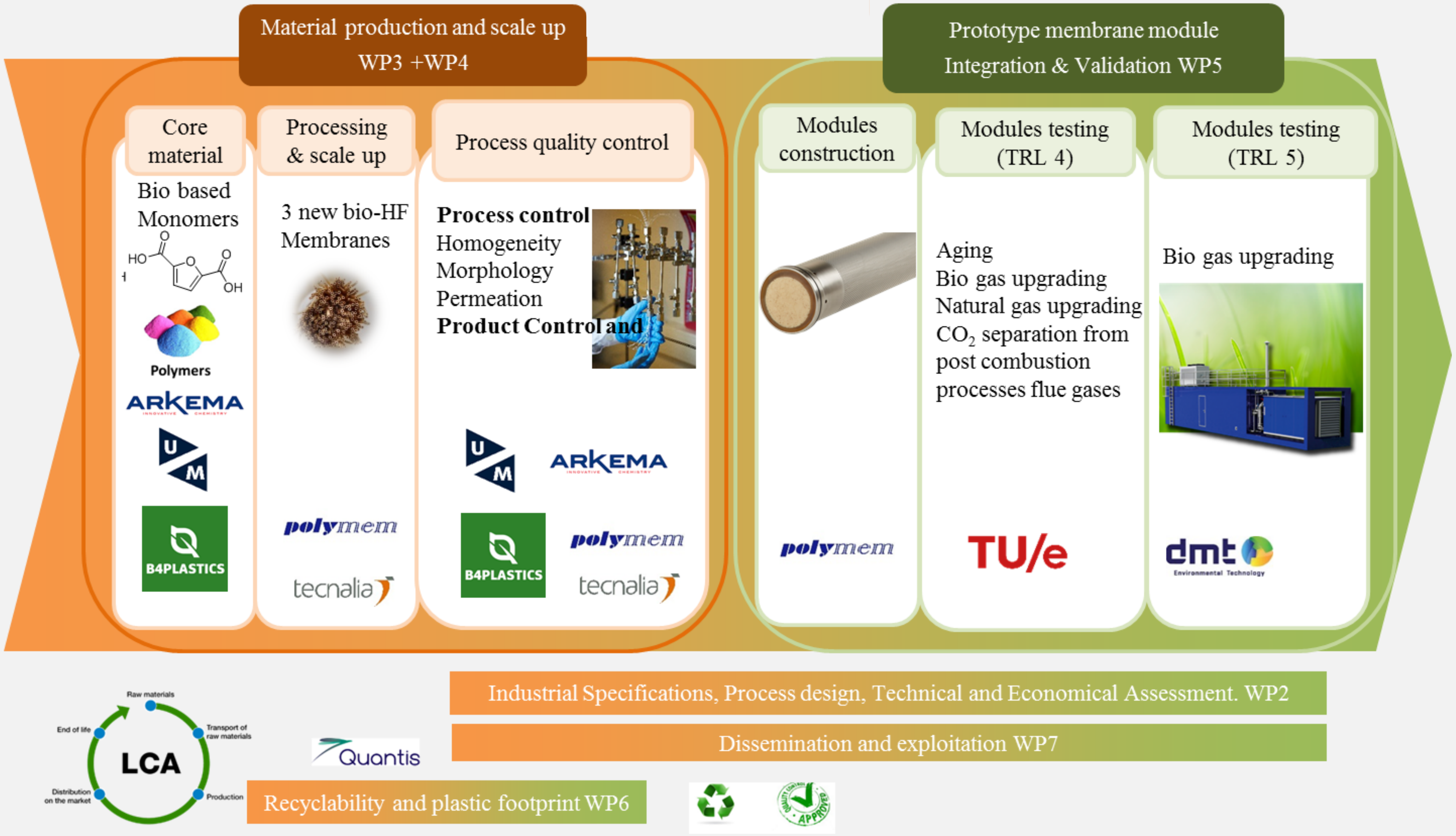


CARMOF is developing a hybrid CO_2 process combining **VTSA modules** based on 3D printed monoliths with thermoelectric regeneration and "in cascade" **membranes system**. The goal is to achieve high purity CO_2 streams from synergetic effects from both technologies

European Commission

Bio-based copolymers for membrane end products for gas separations

BioCoMem



Bio-based Industries Consortium

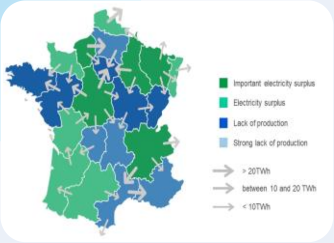
This project has received funding from the Bio Based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme, under grant agreement No 887075.

The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium

C2FUEL Approach: Aligning local supply and demand

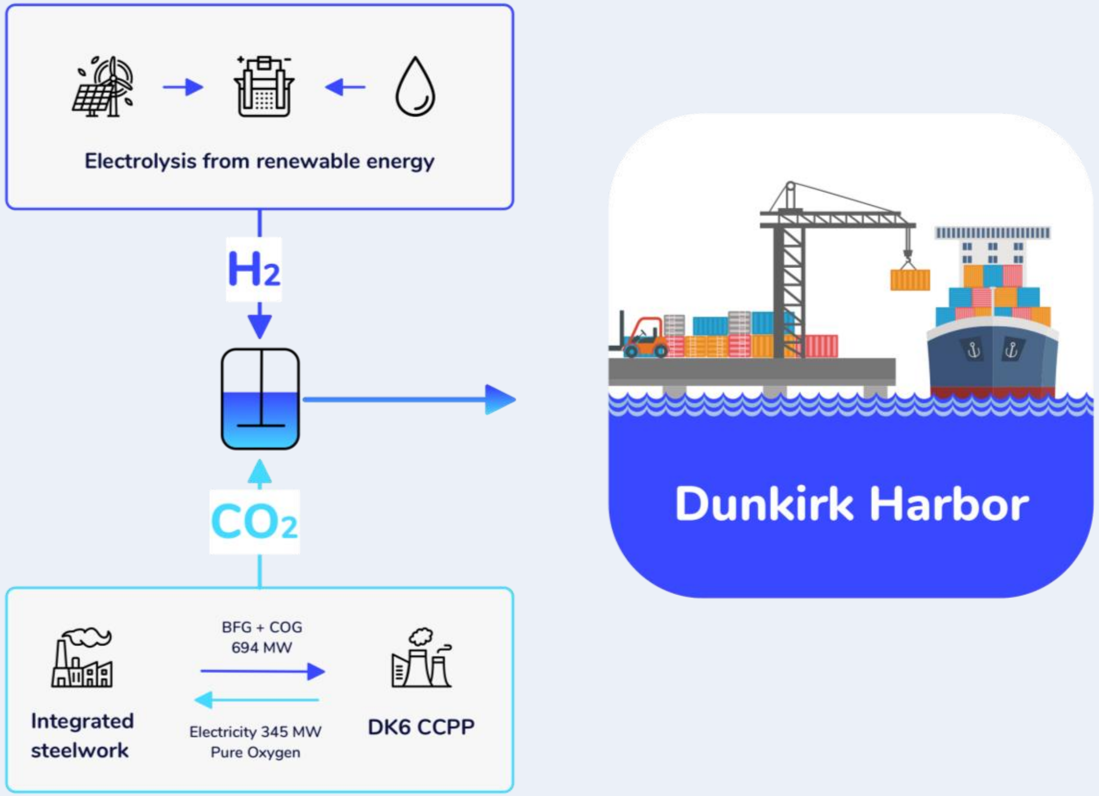
Dr Camel Makhloufi – ENGIE Lab CRIGEN - France

Dunkirk Integrated steel making factory



Large renewable penetration

Dunkirk Harbor



Formic acid as Hydrogen carrier

Decreasing the electricity footprint during boat charging on docks

C2FUEL Output

2,4 million ton of FA

100 000 ton of green hydrogen

1,8 TWh of green electricity

Seasonal storage using 3.6 TWh of renewable electricity

Dimethylether as Maritime and truck fuel

Displacing fossil fuel emission from power plant and decreasing harbor mobility footprint

C2FUEL Output

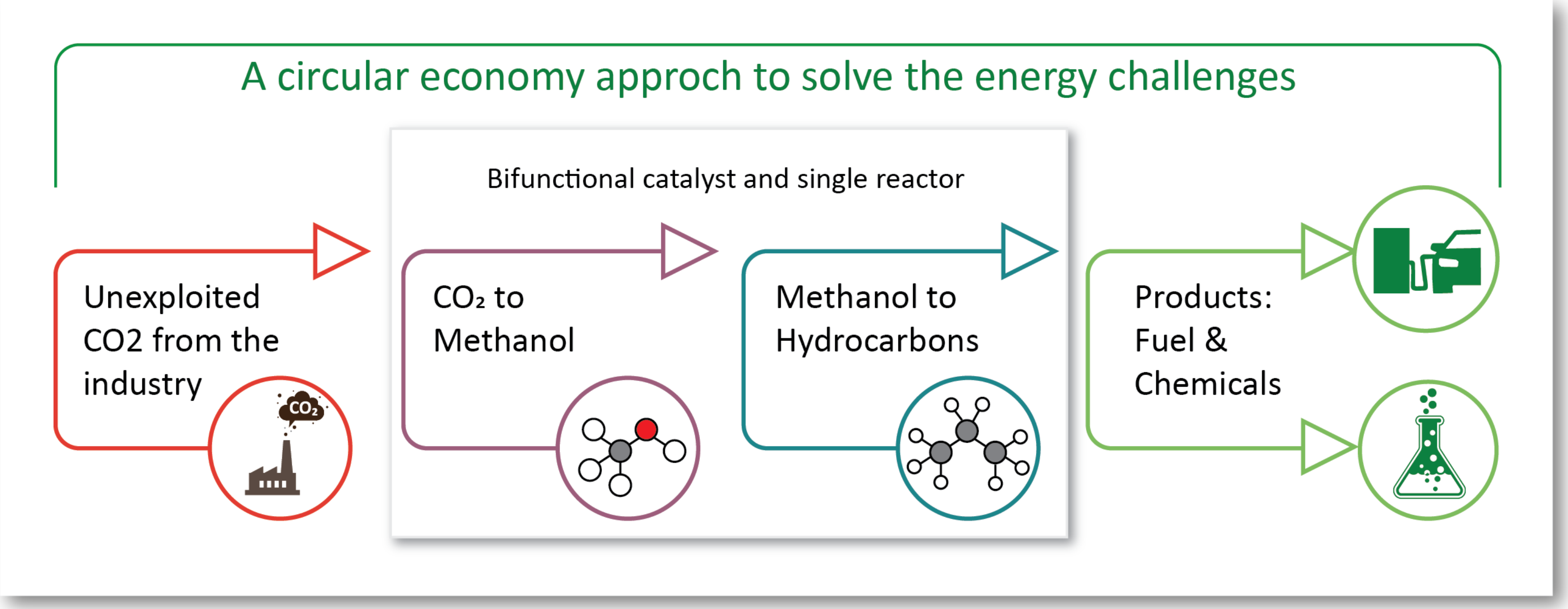
1,2 million ton of DME

320 000 ton of green H_2 produced using 11 TWh of renewable electricity

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 838014".

CO2MOS

Efficient CO_2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS



Unni Olsbye,
University of Oslo,
Coordinator

Other partners

HALDOR TOPSØE
Linde
TATA STEEL
Tüpras
cnrs
جامعة الملك عبدالله للعلوم والتقنية
King Abdullah University of Science and Technology
SINTEF
The University Of Sheffield.
UNIVERSITÀ DEGLI STUDI DI TORINO

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

eCOCO$_2$

Direct electrocatalytic conversion of CO_2 into chemical energy carriers in a co-ionic membrane reactor

AIM: Set-up a technology for direct synthesis of carbon-neutral jet fuels from CO_2 using renewable energy and electrochemical catalytic membrane reactors. Bench-testing targets a 500 W multi-tubular system.

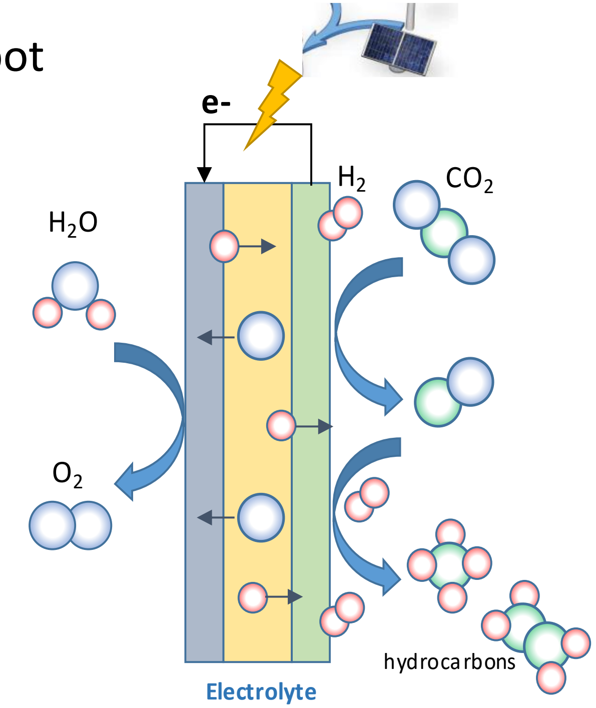
- Single-step electrolysis and one-pot catalytic conversion.
- Operating conditions:
  T = 350-450 °C and > 25 bar.

Product:
Jet fuel

Efficiency:
> 85%

Full integration:
compact sized reactor

Final TRL:
5



Co-Electrolysis Reactor

PARTNERS

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS
COORSTEK
MEMBRANE SCIENCES
ITQ INSTITUTO DE TECNOLOGÍA QUÍMICA
UNIVERSITAT POLITÈCNICA DE VALÈNCIA
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https://ecocoo.eu

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H2020-LC-SC3-2018-NZE-CC | Duration: May 2019 – May 2023 | **EC funding**: 3.9 M€

This project has received European Union's Horizon 2020 research and innovation funding under grant agreement Nº 838077.

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

vito | tecnalia Inspiring Business | Consiglio Nazionale delle Ricerche | ATAE | Hybrid Catalysis | HTF HIGH TECHNOLOGY FILTERS SA | FeyeCon | ECODESIGN company | LCE | LGi sustainable innovation | SOLID POWER | ICI CALDAIE | Petkim

CO₂FOKUS ADVANCING CO₂ CONVERSION

CO_2 utilisation focused on market relevant dimethyl ether production, via 3D printed reactor and solid oxide cell based technologies

Vesna Middelkoop, VITO

1500 N L/h CO_2/H_2 feed, > 30 % CO_2 conversion, 3.5 kW SOE 50 % conversion demo in industrial environment in 2022

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

C4U Advanced Carbon Capture for Steel Industries Integrated in CCUS Clusters

• C[4]U addresses the essential elements for the optimal integration of CO_2 capture in the iron and steel industry as part of the CCUS chain. This spans demonstration of two highly efficient solid based CO_2 capture technologies for optimal integration into an iron and steel plant and detailed consideration of the safety, environmental, societal, policy and business aspects for successful incorporation into the North Sea Port CCUS industrial cluster.

https://c4u-project.eu/

Testing and demonstration of capture technologies at TRL7

WP1: DISPLACE process for reheating ovens

1. Design, construction and commissioning
2. TRL7 N_2-H_2 benchmark demonstration
3. TRL7 DISPLACE technology demonstration
4. Detailed DISPLACE reactor modelling
5. CO_2 purity analysis for pipeline and storage

WP2: CASOH process for blast furnace gas

1. Reactor design modelling
2. Pilot commissioning
3. Screening operating conditions at TRL7
4. Long term experimental testing at TRL7
5. CO_2 purity analysis for pipeline and storage

Integrating CO_2 capture in industrial installations and clusters

WP3: Integration of CO_2 capture technologies in steel plant

1. Detailed CO_2 capture process modelling
2. Techno-economic assessment and optimization of steel mill with CO_2 capture
3. Industrial design and costing of capture systems

WP4: Integration of CO_2 capture in industrial clusters

1. Transport and storage safety impact assessment
2. CCUS cluster whole system modelling and operational logistics
3. Life Cycle Assessment of the North Sea Port CCS cluster

Societal readiness, public policy and the business case

WP5: Societal readiness and public policy

1. System dynamics of socio-economic and political aspects
2. Assessment of concerns and needs of societal stakeholders
3. Policy instruments assessment for CCUS in industrial clusters

WP6: Long term business models

1. Market and stakeholder analysis
2. Scenario development, investment and risk analysis
3. Customer value proposition development
4. Business model descriptions

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 884418.

Project Coordinator
Haroun Mahgerefteh
University College London
h.mahgerefteh@ucl.ac.uk

Project Period
April 2020 - March 2024

Overall budget
€ 13,845,496

Demonstrating a refinery-adapted cluster-integrated strategy to enable full-chain CCUS implementation – REALISE (May 2020 – April 2023)

CO_2 capture with 2nd gen. solvents

- Mobile pilot on-site refinery
- Stationary pilot

Solvent management technologies

- Avoid solvent loss
- Emissions control

CO_2 transport, conversion and storage

- CO_2 liquefaction
- CO_2 conversion
- CO_2 storage

Societal study

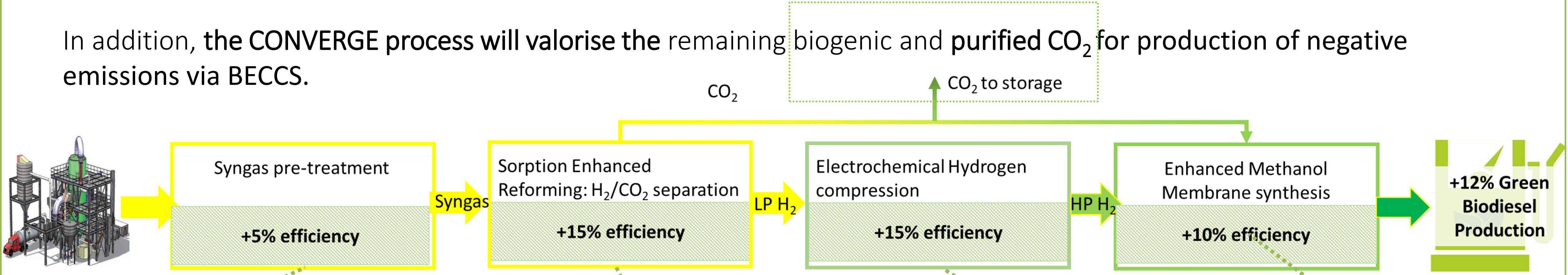
- EPE program
- CCUS readiness

CCUS business cases: Irland, China, S. Korea

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884266

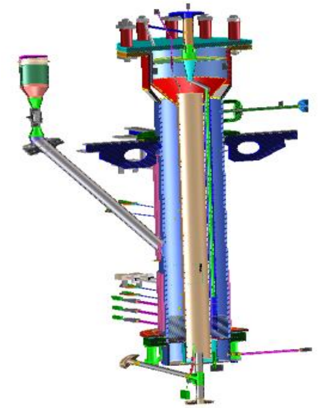
The **CONVERGE project will validate an innovative process** which will **increase the biodiesel production by 12%** per secondary biomass unit used and **reduce the CAPEX by 10%.** The **CONVERGE technologies will be validated** for more than **2000 cumulated hours** taking these from the discovery stage (TRL3) to development stage (TRL5).

In addition, **the CONVERGE process will valorise the** remaining biogenic and **purified CO_2 for production of negative** emissions via BECCS.

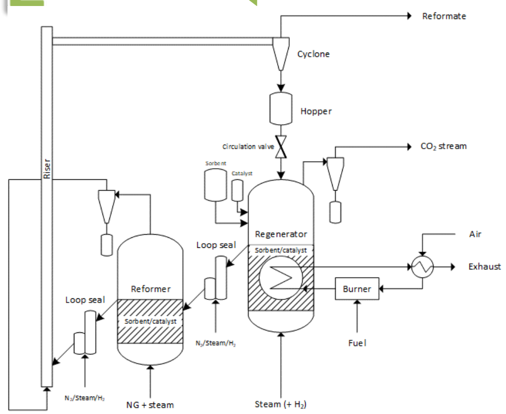


Biomass gasification

CarbON Valorisation in Energy-efficient Green fuels

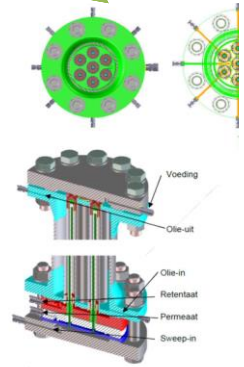


Catalytic cracking reactor



Sorption Enhanced Reformer

Electrochemical Hydrogen compressor

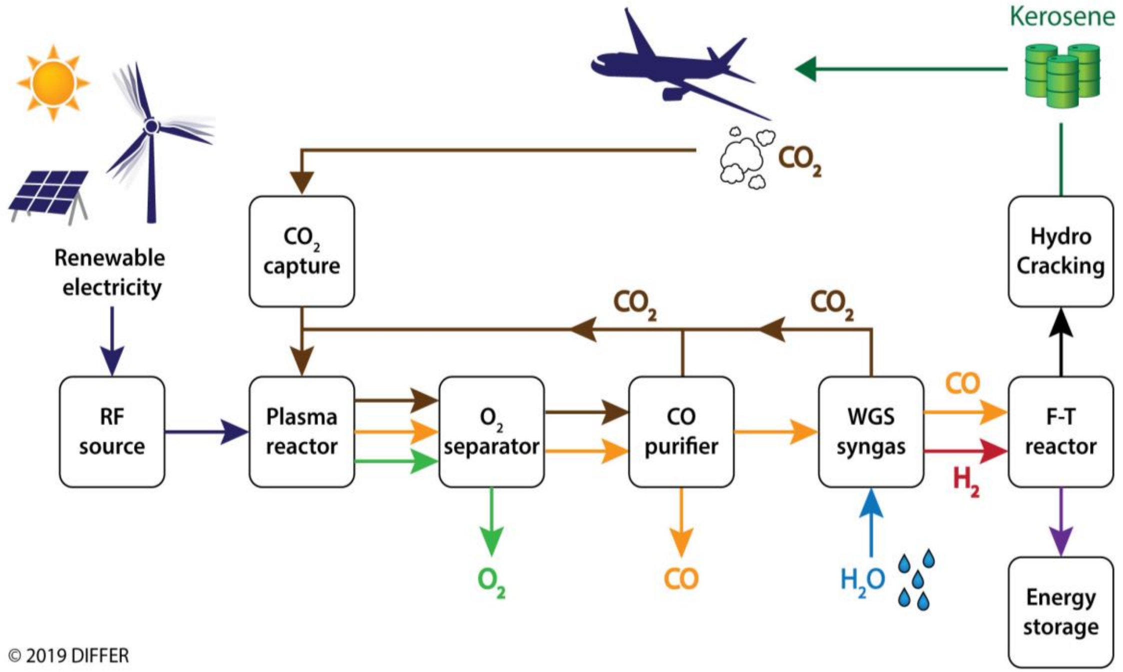


Membrane reactor

Methanol membrane reactor

The CONVERGE project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 818135

www.converge-h2020.eu

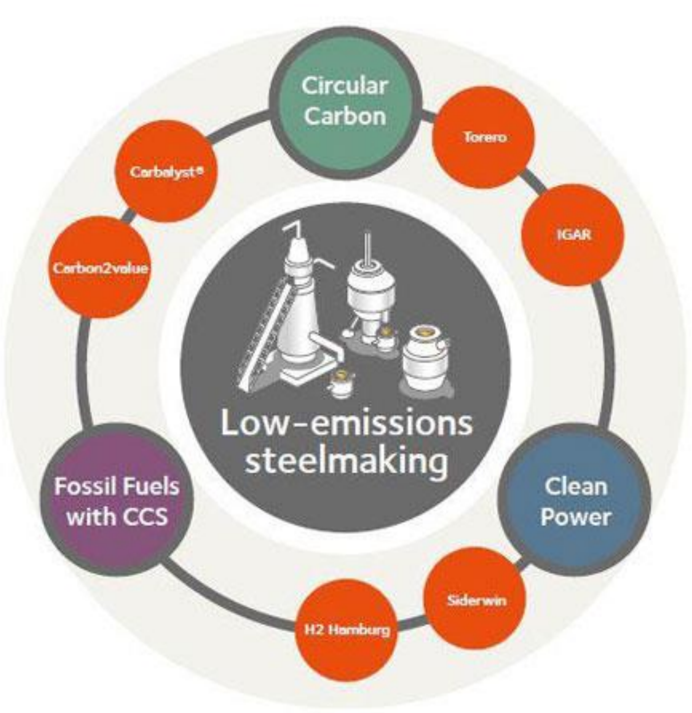


The KEROGREEN CO_2 plasma route to CO and alternative fuels

M.N. Tsampas, DIFFER, The Netherlands

Kerogreen aim: Demonstation of the full chain process from renewable, electricity, CO_2 (captured) and H_2O to kerosene.

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



ArcelorMittal

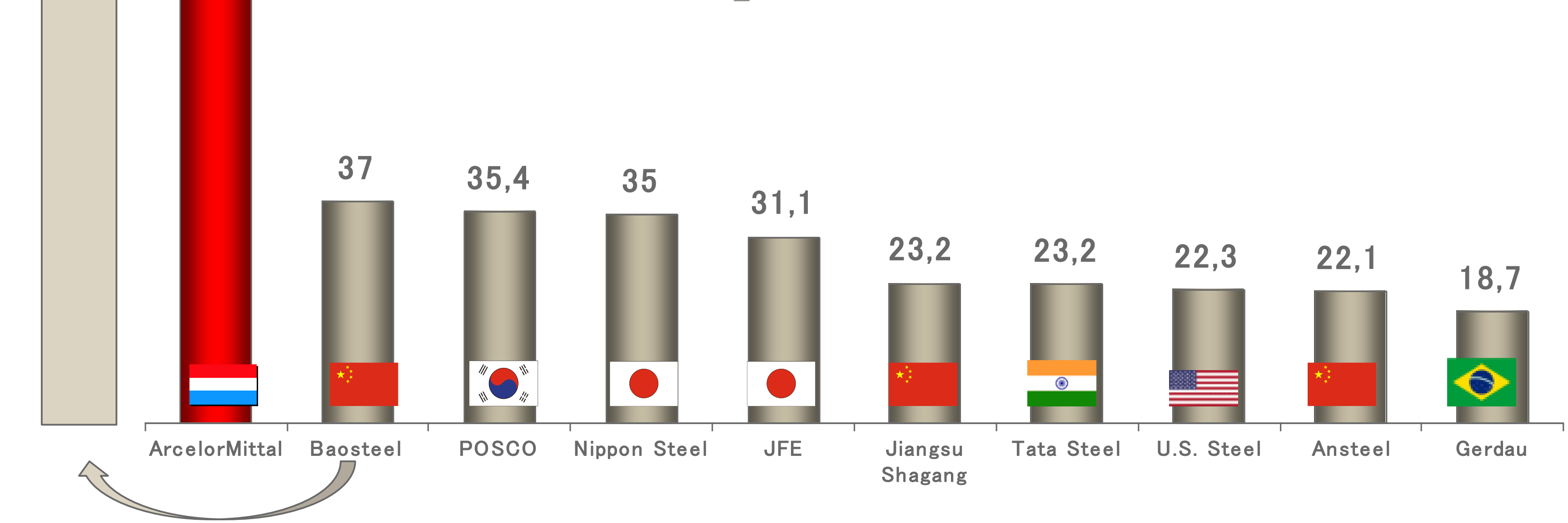
ArcelorMittal : possible pathways towards

THE LOW EMISSION PLAN(T)

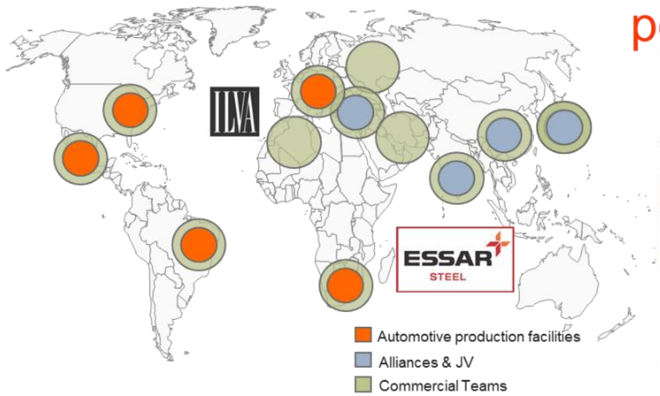
July 2020

Largest steel producers
(in mt crude steel)

ArcelorMittal



ArcelorMittal's industrial and commercial network



Mining business portfolio

* Source: Worldsteel

Group Management

Lakshmi N. MITTAL
President of the Board

Aditya MITTAL
Chief Executive Officer
(CEO)

CTO

Pinakin CHAUBAL

Emerging Technology Deployment

Carl De Maré

LIS team = low impact steel making

eternal

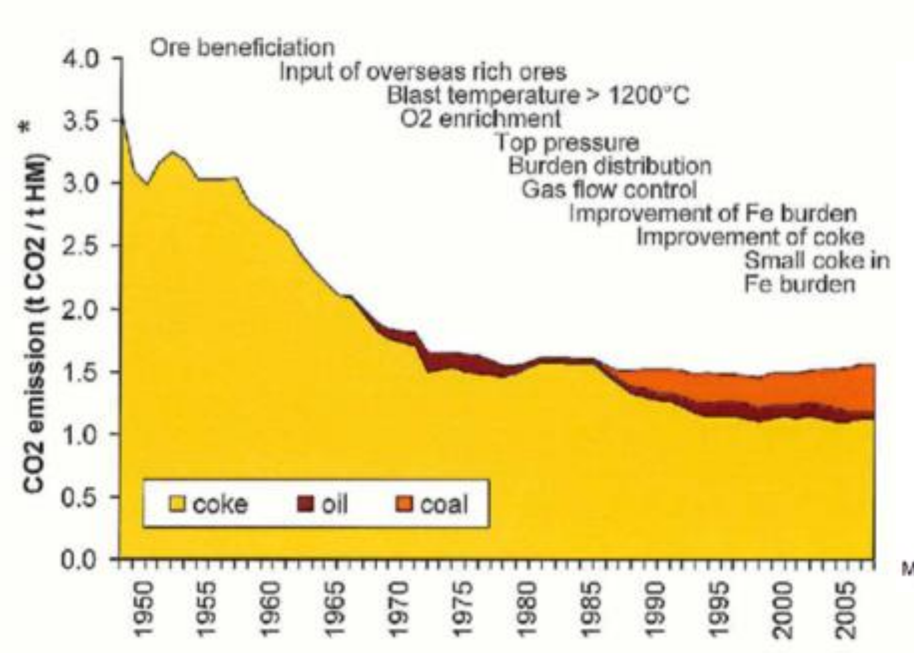
Agenda :

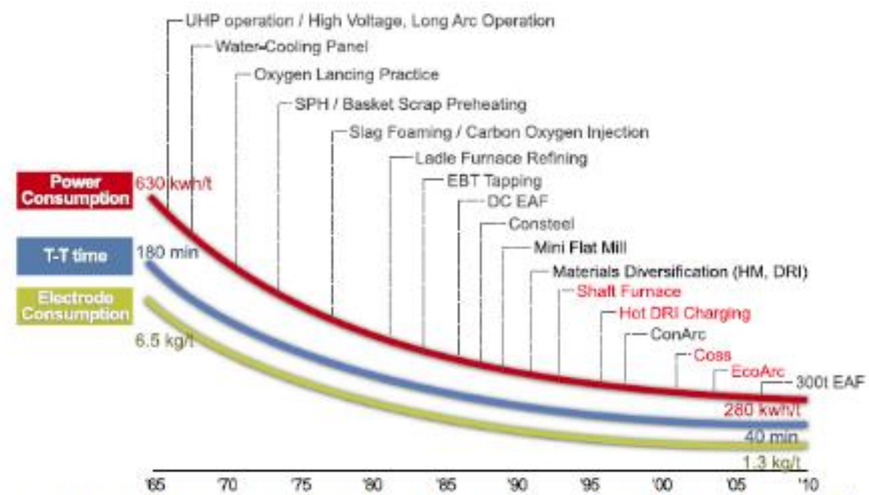
1. European history of steelmaking
2. Others are still at the very beginning of this history
3. What can Europe afford ?
4. Low emission principles
   a) Gas separation
   b) CO re-use by chemical industry
   c) CO_2-H_2-chemistry : new technologies
   d) CO_2 sale
   e) CO_2 storage
5. Some political issues

The challenge of the steel industry = C-footprint reduction

ArcelorMittal

Conventional steel making = blast furnaces (BF) Electrical steel making = electric arc furnaces (EAF)





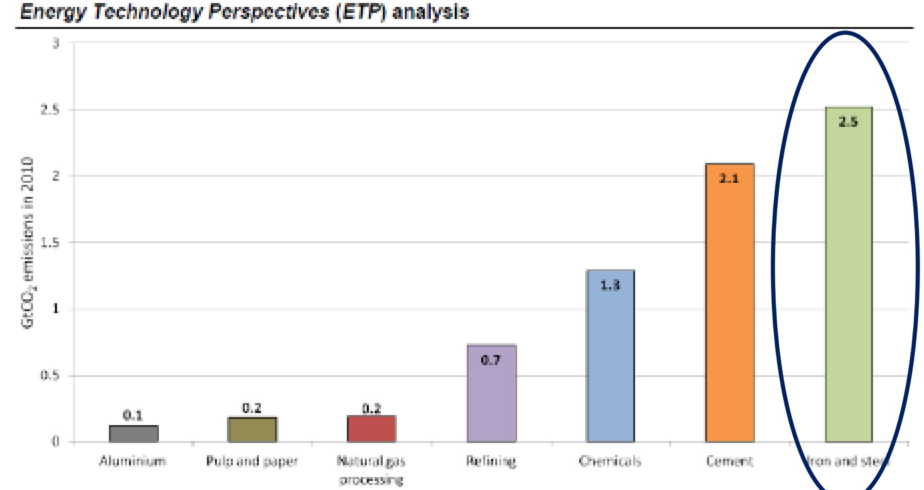
Major technology developments in the EAF as a function of time (year). Adapted from Toulouevski and Zinurov.[4]

1,8 billion tons of steel in 2018

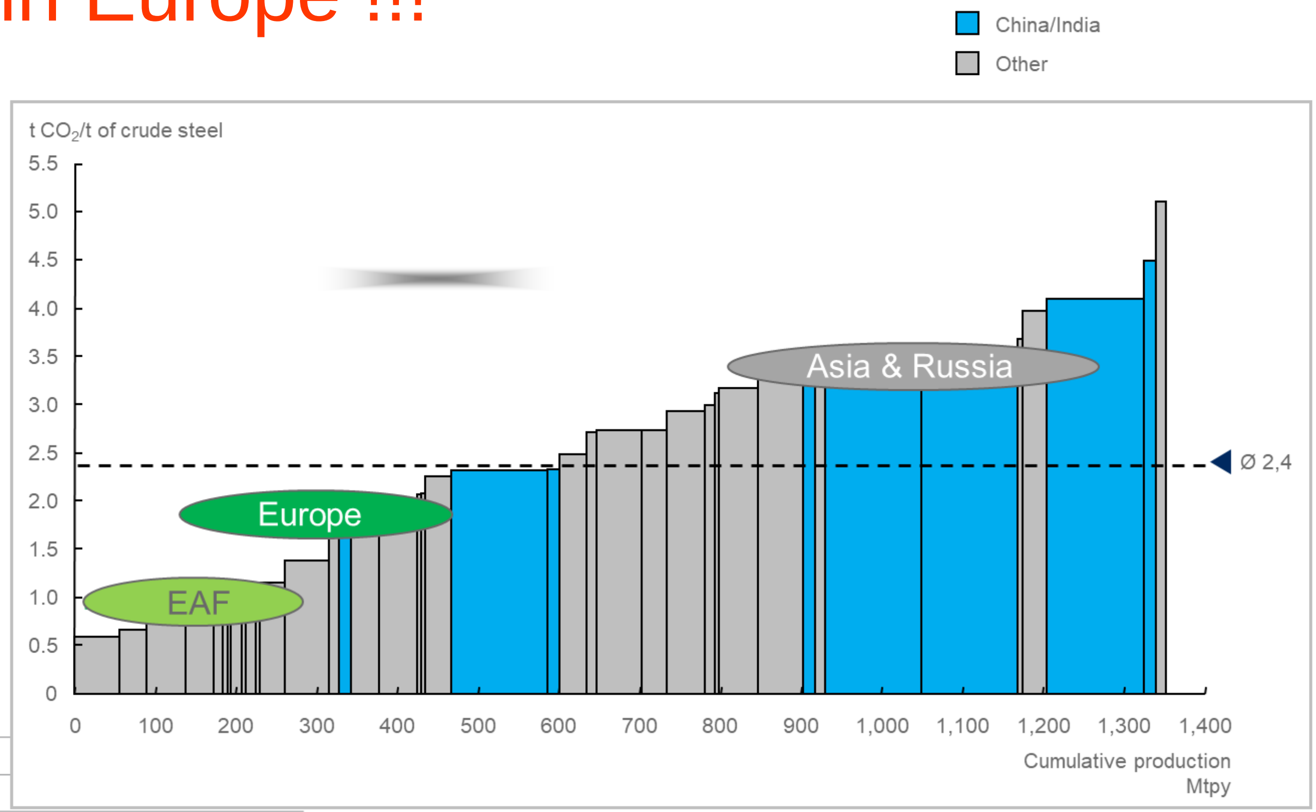
30% of industrial CO_2-emissions.
6,7% of anthropogenic CO_2-emissions

They are amongst the highest of industries….

Figure 1. Global emissions from the seven most CO_2-intense industrial sectors in the IEA *Energy Technology Perspectives* (*ETP*) analysis



C-footprint reduction : the main emittors are not located in Europe !!!



global CO_2 curve

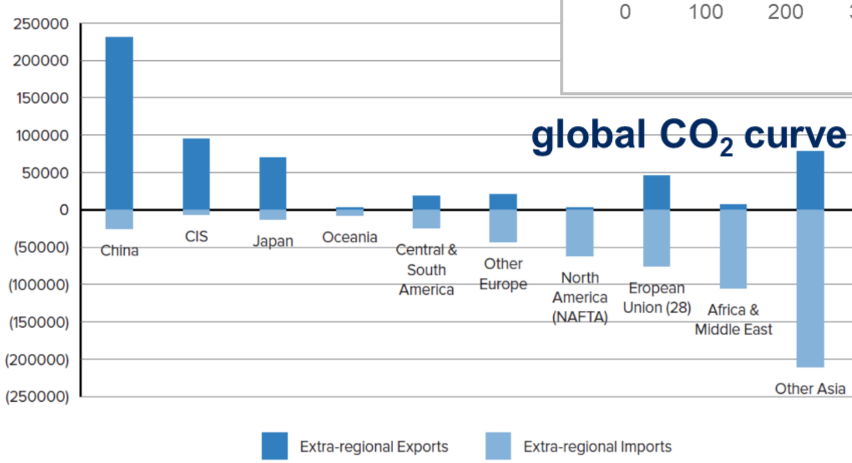


Figure 3.1.2. World trade of carbon embodied in commodity steel by region (kton CO_2) in 2016

AM decarbonation plan : -30% by 2030, carbon neutrality by 2050

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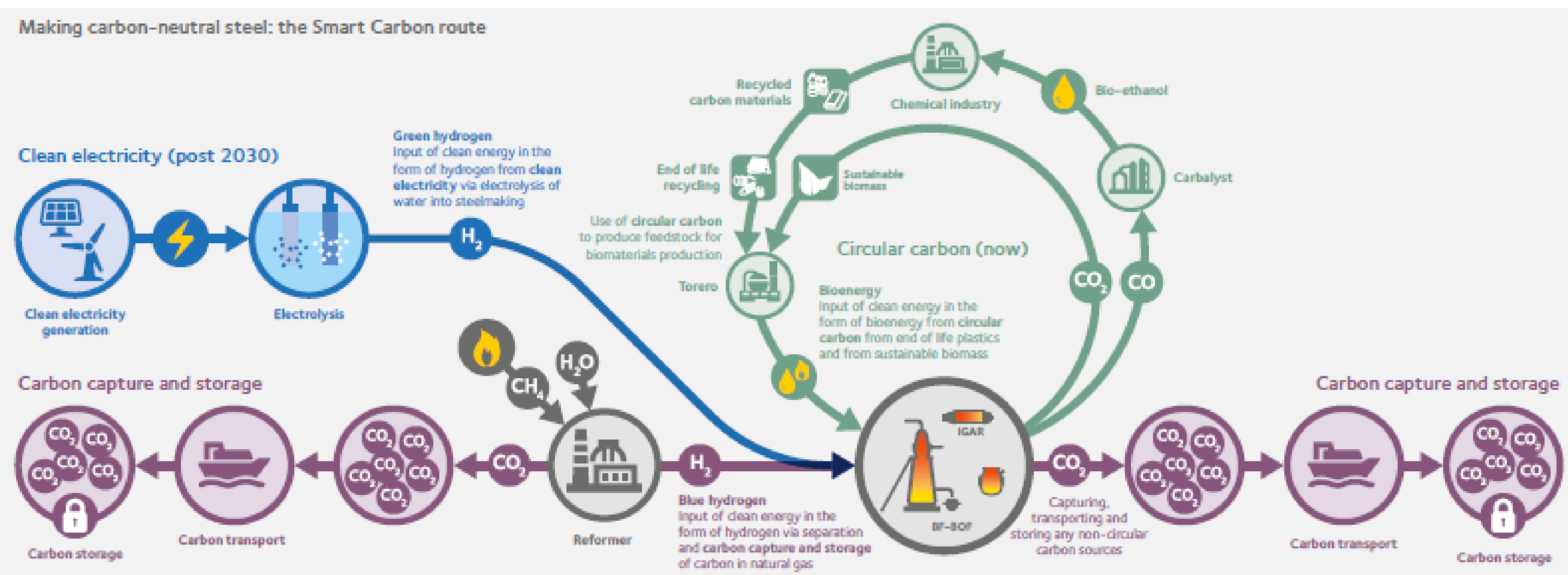
Several measures to be developed :

- Energy efficiency and recovery
- Maximum use of affordable renewables (scrap melting) and C-free hydrogen (DRI)
- Use of biomass
- Use of circular carbon products (e.g. waste plastics)
- Re-use of carbon emissions (CCU)
- Storage of carbon emissions (CCS)



AM decarbonation plan : biogenic carbon : free of CO2 allowances, is available in small volumes, e.g. waste wood….

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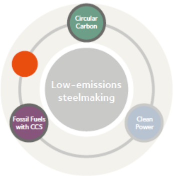
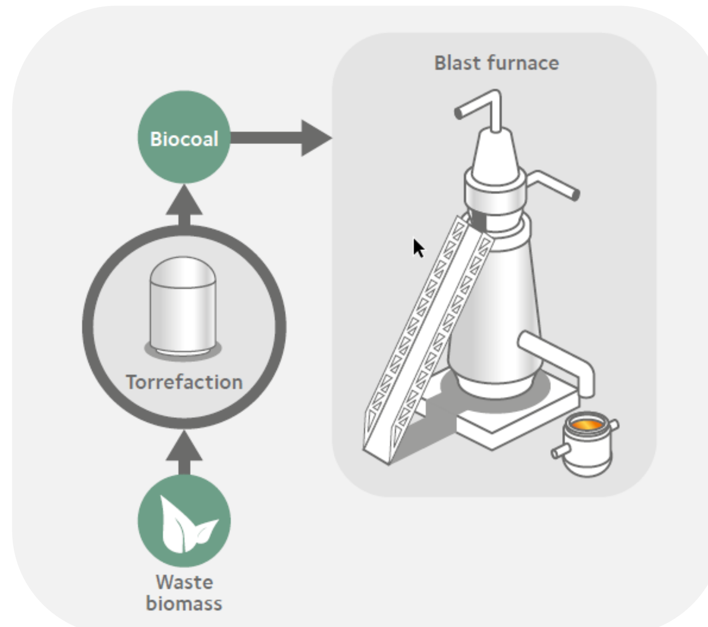


Circular Carbon – Upgrading waste wood into "Bio-Coal" and plastics into circular carbon

Torero
Fueling a sustainable future



Torero – 30m€ demo project to convert 120.000 ton waste materials into "bio-coal" in ArcelorMittal Gent

Carbon can be re-used :

European Commission

Scientific Advice Mechanism (SAM)

Novel
carbon capture and utilisation
technologies

Group of Chief Scientific Advisors
Scientific Opinion 4/2018

Scientific Opinion
Novel Carbon Capture and Utilisation Technologies

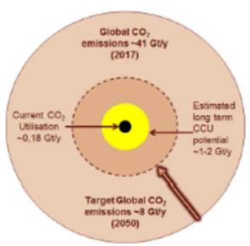


Figure 8 – Global CO_2 emissions and the role of CCU. The figure shows also the target global emissions for 2050 as well as a simplified estimation for the CCU potential including all the possible uses (simplified and adapted[21,22]).

CORESYM

CarbOn-monoxide RE-use through industrial SYMbiosis between steel and chemical industries

CORESYM

CarbOn-monoxide RE-use through industrial SYMbiosis between steel and chemical industries

CO-rich waste gases can be converted into products with a reduction of CO_2 emissions and other negative impacts.

Using waste gases as a feedstock, instead of for energy, can result in emission reductions from the production of energy and products of up to 21-34% compared to the baseline. In addition, the process of cleaning up waste gases for use as a feedstock also results in a concentrated stream of CO_2, which lends itself to Carbon Capture and Storage (CCS). While roughly a third of the direct emissions from waste gases can be mitigated through use as a feedstock, an additional third is made capture ready in the process. If CCS is implemented alongside waste gas recycling at a European scale, this could result in a reduction of up to 3% of European CO_2 emissions. In addition to reducing CO_2 emissions, when substituting waste gases for biobased feedstocks, water demands, wastewater production, and land use reduced, with positive implications for biodiversit

Centre for Low Carbon Futures

ArcelorMittal

recent Risk Management position paper (DNV, 2011) states that using a variety of carbon utilisation technologies can potentially reduce annual CO_2 emissions by 3.7 Gt. This equates to approximately 10% of current annual CO_2 emissions. A 10% replacement of building materials by CO_2 captured in stable minerals would reduce CO_2 emissions by 1.6 Gt

CCS is the only option to decarbonise many industrial sectors. CCS is currently the only large-scale mitigation option available to cut the emissions intensity of production by over 50% in these sectors.

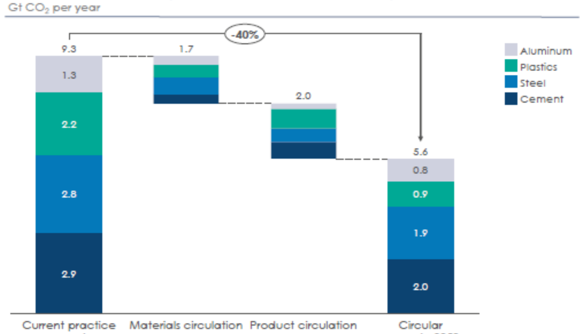
Take home message

Trading renewable energy by using CO_2 has a potential impact on mitigation of climate changes of over 7 Gtons CO_2 equivalent.

Green Energy Trading

CO_2 uses	Existing (future) CO_2 demand (Mt per h)
Enhanced oil recovery	30–300 (<300)
Urea	5–30 (<30)
Food and beverage	~17 (35)
Water treatment	1–5 (<5)
Other	1–2 (<6)
Enhanced coal bed	
Methane recovery	(30–300)
CO_2 concrete curing (MC)	(30–300)
Algae cultivation	(>300)
Mineralisation (MC)	(>300)
Red mud stabilisation (MC)	(5–30)
Baking soda (MC)	<1
Liquid fuels (methanol, formic acid)	(>600)

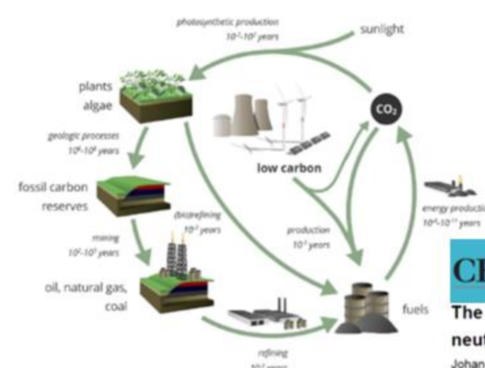
A more circular economy can cut emissions from the harder-to-abate sectors in industry by 40% by 2050



Source: Material Economics analysis for the Energy Transitions Commission (2018)

nova Institute for Ecology and Innovation

Hitchhiker's Guide to Carbon Capture and Utilisation



CHEMSUSCHEM

The Chemical Route to a CO_2-neutral world

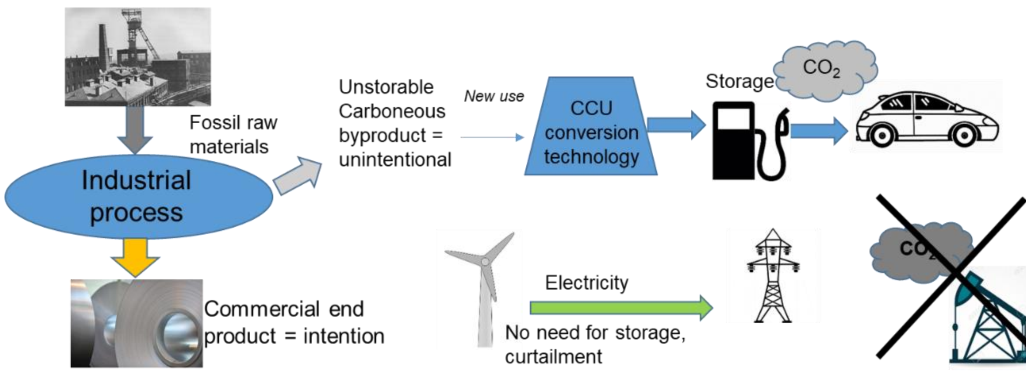
Johan A. Martens,[a] Annemie Bogaerts,[b] Norbert De Kimpe,[c] Pierre A. Jacobs,[a] Guy B. Marin,[d] Korneel Rabaey,[e] Mark Saeys[d] and

The Low Emission Plant principles

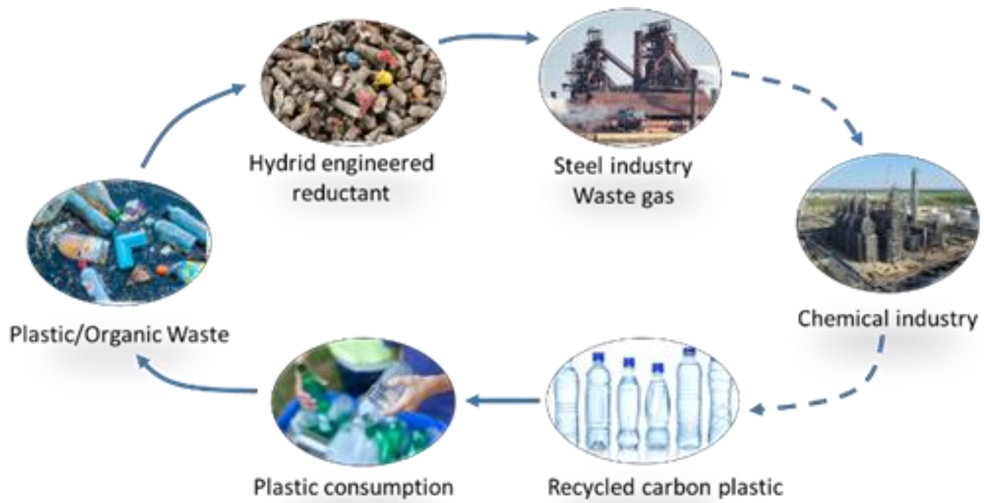
ArcelorMittal

Technical principles :

•Half of the steel mill gases is CO, which is burnt for power production. By not burning the CO a lot of CO_2 is avoided.
This CO can be used for fuel and chemical production.
•The lack of electricity on the grid, can be compensated by the production of RENEWABLE electricity. This is the major lever to reduce the CO_2 emissions
•By separating the CO from the CO_2, pure CO_2 is available for re-use or storage.



Only the re-use of C can ignite a CIRCULAR economy



The different steps of the Zero Emission Plan(t) concept of ArcelorMittal

ArcelorMittal

Steel mill gas

Gas separation

CO (+ H_2) re-use

CO_2 + H_2 re-use

CO_2 fixation

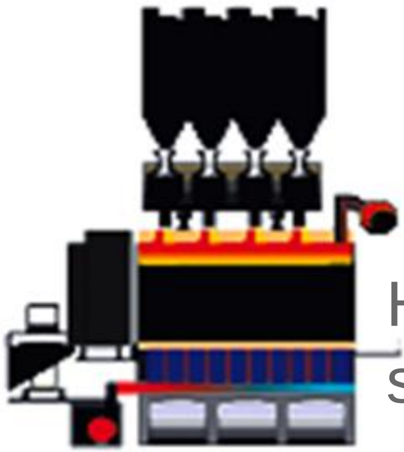
CO_2 storage

Circular economy

The steel mill of the future …. will still produce gasses

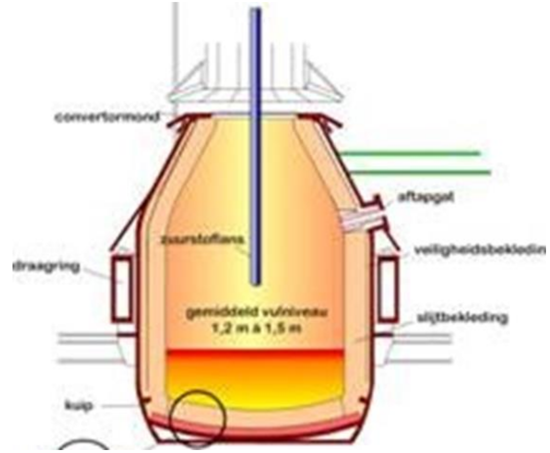
ArcelorMittal

Coke Oven gas



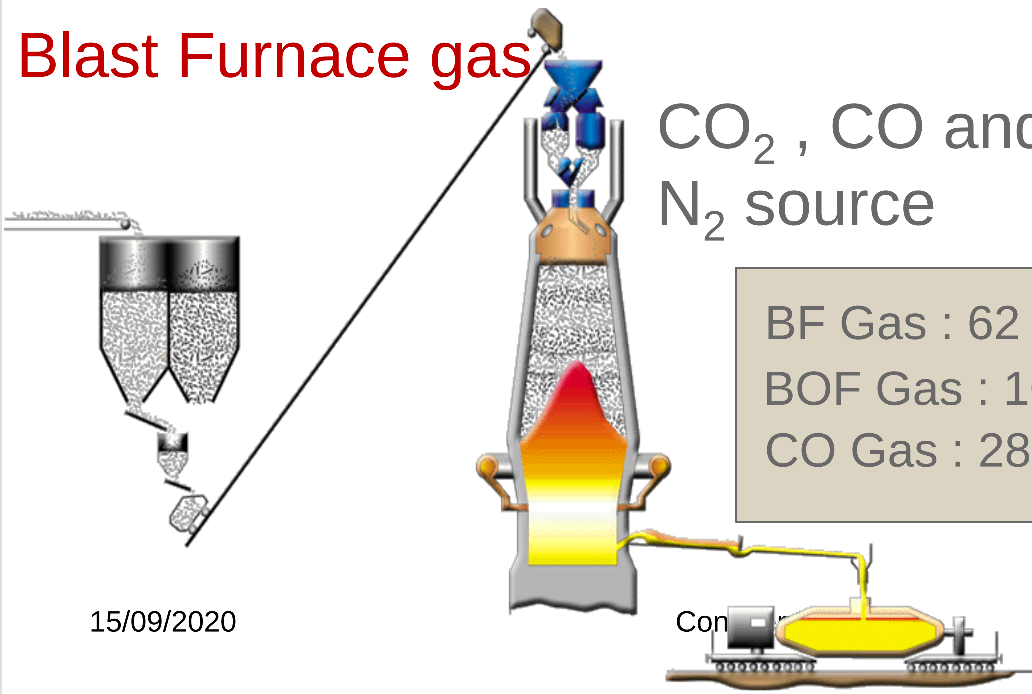
H_2 and CH_4 source

Basic Oxygen Furnace gas



CO source

Blast Furnace gas



CO_2 , CO and N_2 source

BF Gas : 62 % BOF Gas : 10% CO Gas : 28%	52% of the gas energy replaces natural gas in the plant Power plant : 48%

Peak name

Benzene
Toluene
Ethylbenzene
p-Xylene
m-Xylene
o-Xylene
DCPCD
Styrene
Ethylacetylene
Vinylacetylene
Hydrogensulfide
Corbonylsulfide
Methylmercaptan
Carbondisulfide
Thiophene
Ethane
Ethylene
Propane
Propylene
iso-Butane
n-Butane
Acetylene
trans Butene-2
1-Butene
iso-Butene
cis Butene-2 + Neopentane*
n-Pentane
Butadiene 1-3
Methyl Acetylene

The steel mill of the future …. will provide the single gas components

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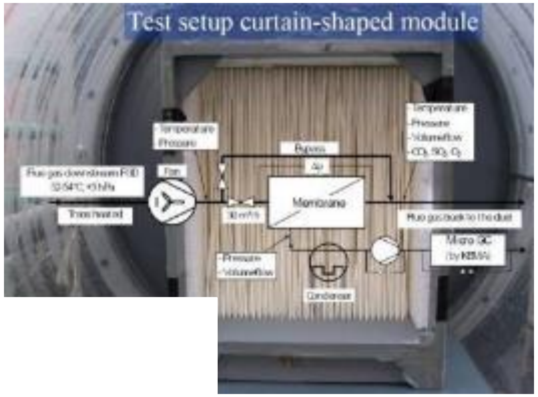
Steel mill gases
$CO/CO_2/H_2/N_2$

DMEA
Solvents

(V)PSA

AM Saldanha Works VPSA



MEMBRANE

15/09/2020

The steel mill of the future …. will provide the single gas components

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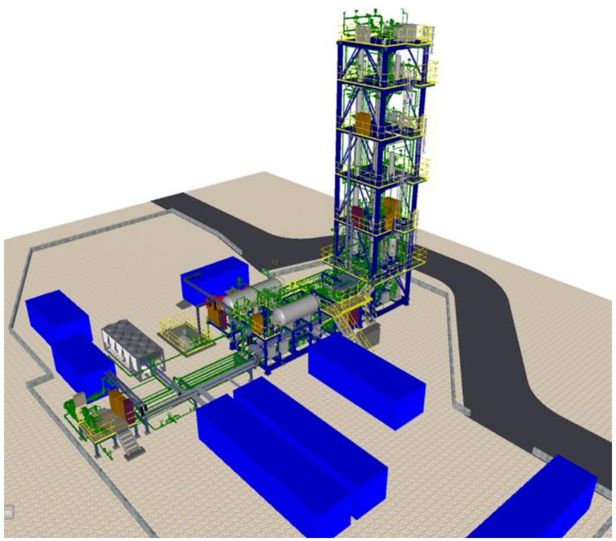
3D : pilot project 2019 – 2023 (Dunkirk)

pré-FEED done by IFPEN

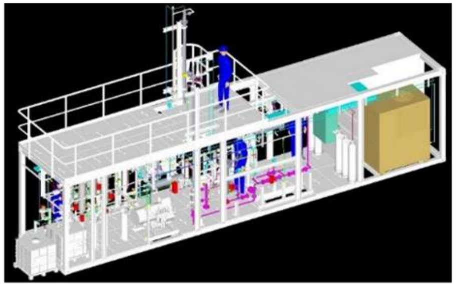


VALORCO

IFPEN mini-pilot in Solaize

Carbon2Value : pilot project 2018 – 2020

INTERREG sponsored project

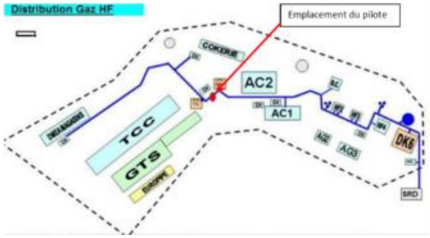


GENESIS : pilot project 2019 – 2021

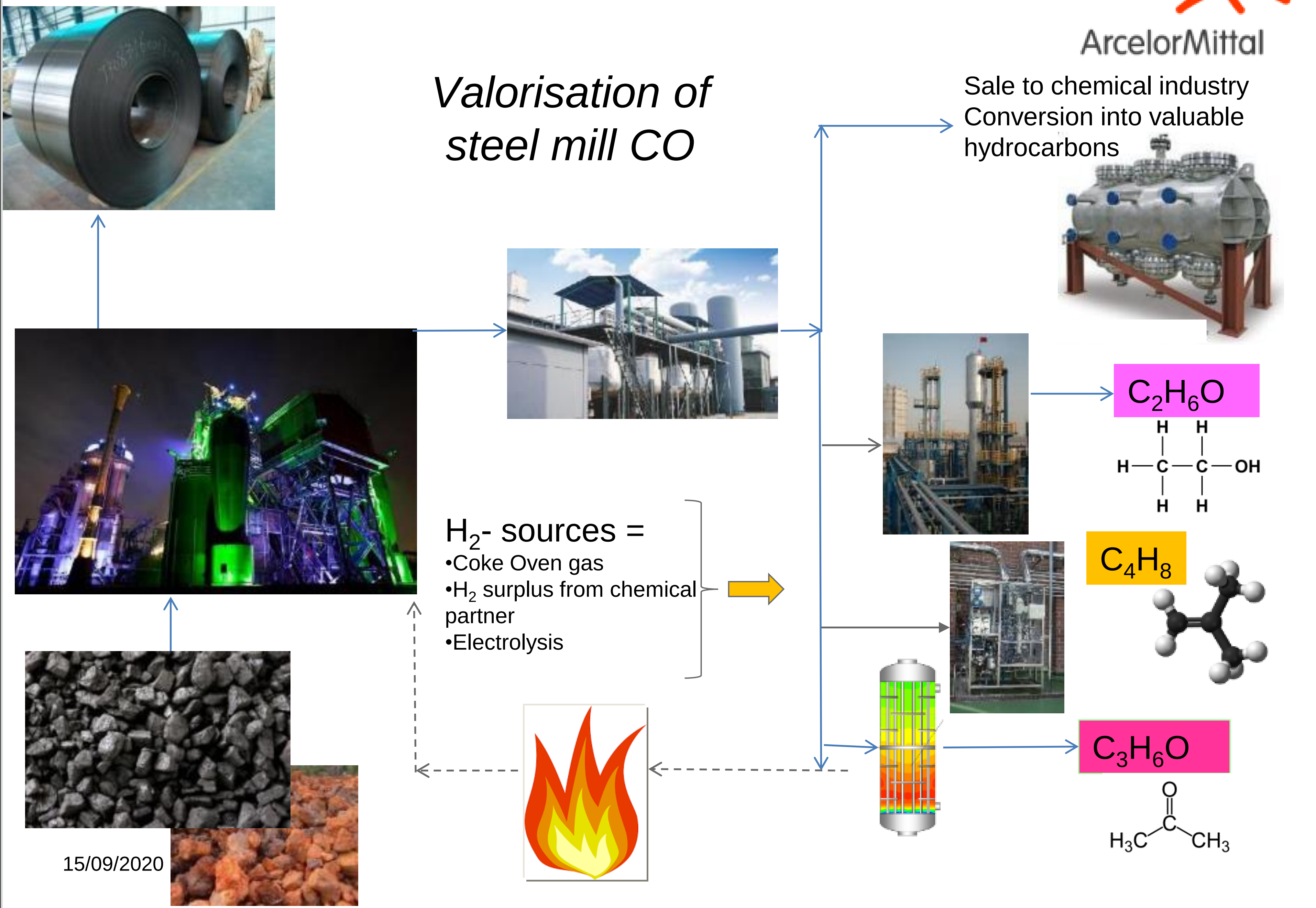
Membrane separation : genesis

Capture of 0,5 t/h CO2 from 1.100 Nm³/h BF-gas to study feasability

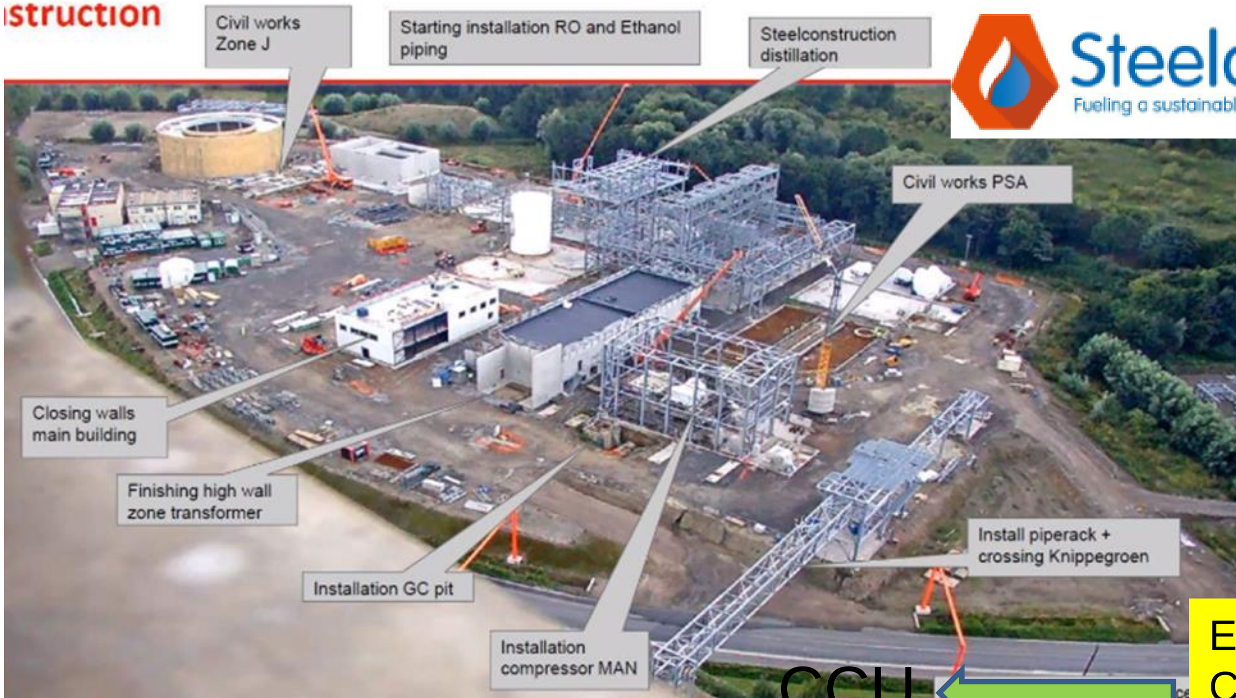
IFP Energies nouvelles



The steel mill of the future …. will sell CO

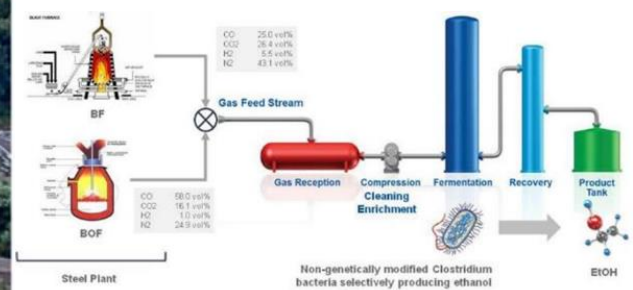


The steel mill of the future …. will sell CO



Steelanol
Fueling a sustainable future

The Gent Ethanol plant



CCU

CCS

EtOH production = X T/y
CO_2 avoided = 2,1 X T/y
CO_2 captured = 6,6 X T/y
Total CO_2 = 8,7 X ton/y

Potential of 300 kton EtOH/year = 380 Ml/year= over 700 kT/y of CO_2 savings

Shougang Commercial Plant

The steel mill of the future …. will sell CO

Rijksdienst voor Ondernemend Nederland

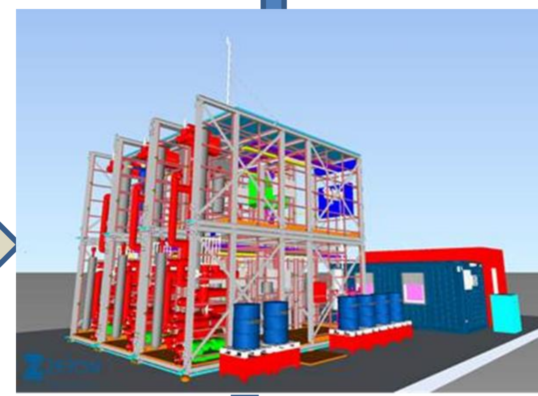
CAPEX = 10% of investment cost of wind energie, for the same CO_2 saving

CO_2/H_2S-Gas

Steam for CO_2 stripping

CO gas

100 % yield
CO_2 scrubbing
H_2S scrubbing
Energy consumption = 2,6 GJ/tCO_2



BF gas

SCF reactor tail gas

Synthetic Cracker Feed

Institute for Sustainable Process Technology

ISPT

H_2 import gas

CCU
CCS

SCF production = X T/y
CO_2 avoided = 2,9 X T/y
CO_2 captured = 4,3 X T/y
Total CO_2 = 7,2 X ton/y

The steel mill of the future …. will sell CO_2 - derivates

ArcelorMittal

Valorisation of steel mill CO_2

Fuels - chemicals

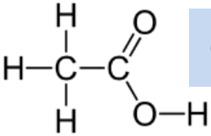
Raw CO_2

H_2- sources =

- Coke Oven gas
- H_2 surplus from chemical partner
- Electrolysis

CH_4

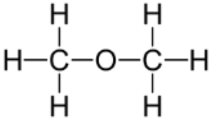
$C_4H_8O_2$

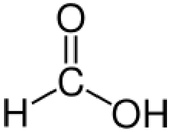


CH_3COOH + C_2H_6O

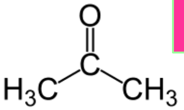
H_3COH

H_3COCH_3

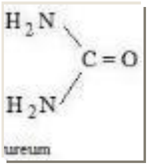


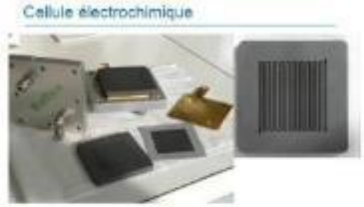


CH_2O_2



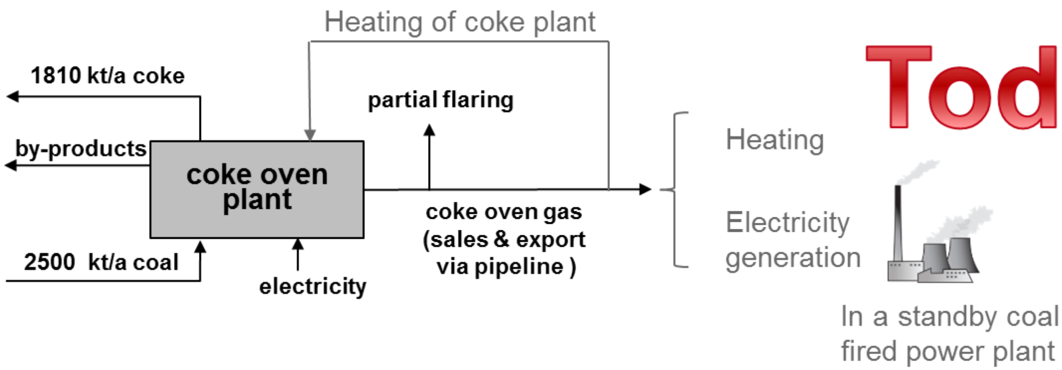
C_3H_6O





The steel mill of the future …. will sell CO_2 - derivates

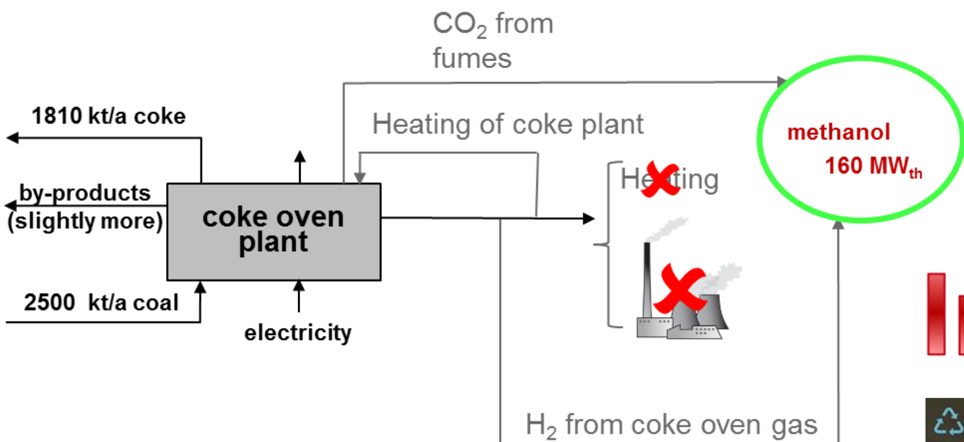
ArcelorMittal



Today

CO_2 VALORCO

https://www.carbonrecycling.is/news/co2-to-methanol-plant-china



recycled carbon transport fuel

Shuncheng Steel China

In Future

Chinese chemicals corporation Henan Shuncheng Group has signed an agreement with Icelandic technology developer Carbon Recycling International – CRI hf., to design a plant based on CRI's technology that will produce low carbon intensity methanol in China. The agreement was signed at CRI's headquarters with his excellency Mr. Jin Zhijian, ambassador of the People's Republic of China to Iceland in attendance. Total cost of the project is estimated around USD 90 million (10 billion ISK).

The new Shuncheng plant, which will be built in Anyang city, Henan province of China, will recycle about 150,000 metric tons of CO2 per year, with other waste gases to produce 180,000 tons of methanol and LNG annually. The amount of CO2 recycled equals the annual emissions of 40,000 cars.

MeOH production = X T/y
CO_2 avoided = 1,3 X T/y → CCU
CO_2 captured = (1,3 X T/y) → CCS
Total CO_2 = 1,3-2,6 X ton/y
+ additional PP closure
Total CO_2 = 7 X ton/y

onfidential

The steel mill of the future …. will sell CO_2 - derivates

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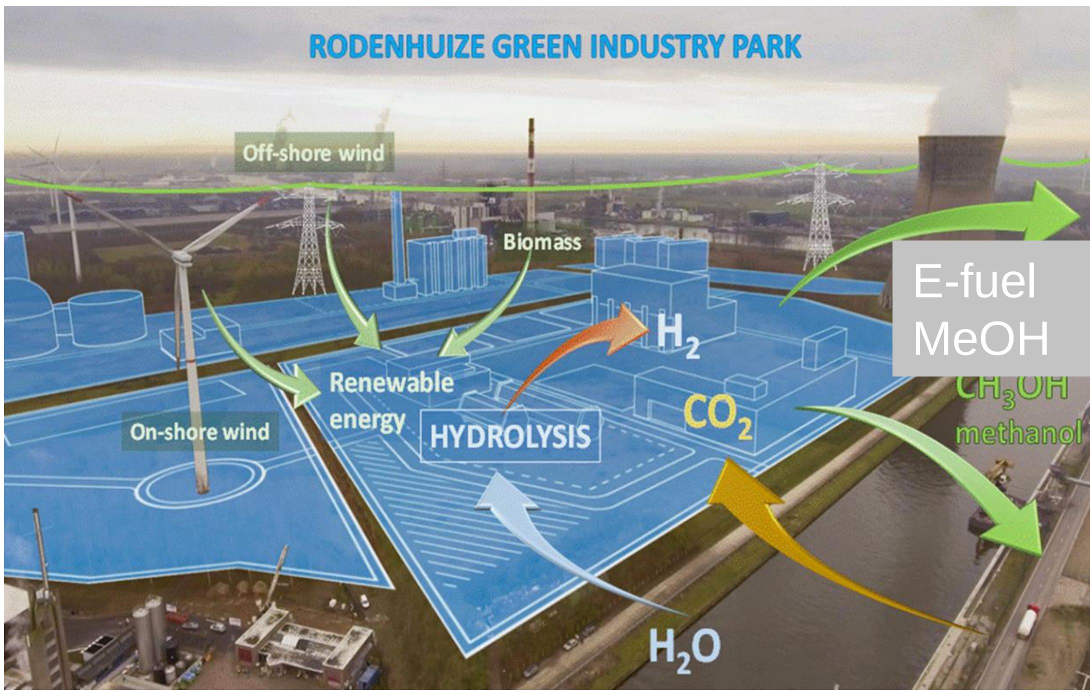
RODENHUIZE - DEMONSTRATIEPROJECT CCU

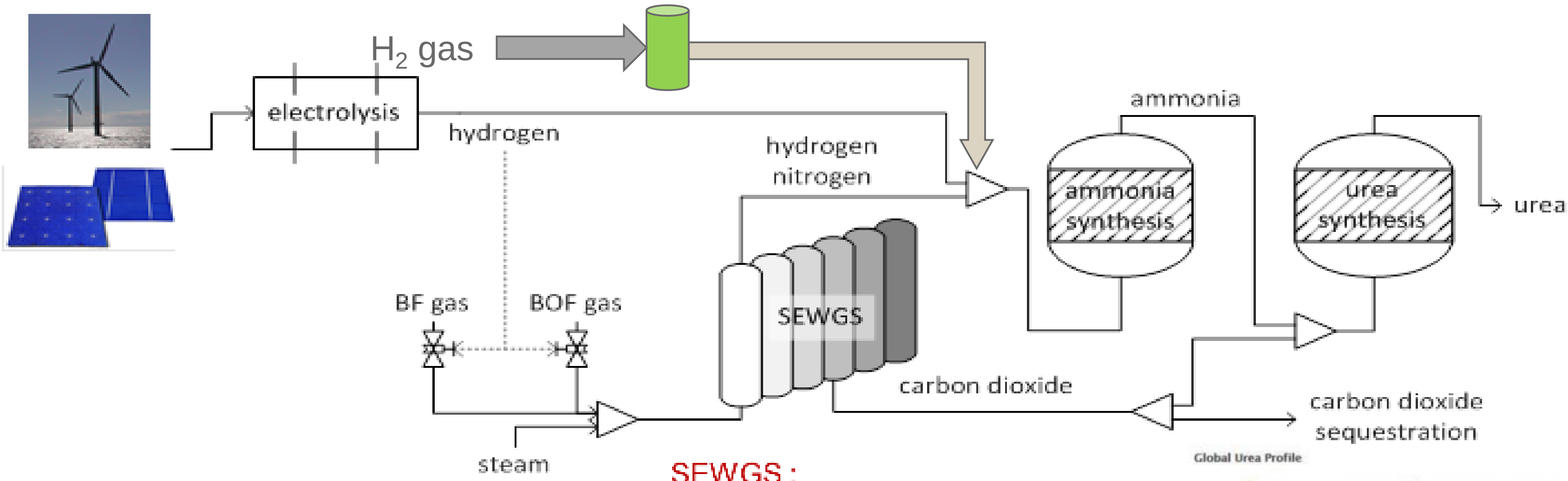
565 MW
Methanol
Ureum-formaldehyde
Formic Acid
H2 & MeOH Transport
2030

300 MW
Methanol
Biodiesel
Methylamines
Ammoniak
Methylamines
2027

55 MW
Methanol
Biodiesel
2023



In integrated steel mills .. a combination of gases can be used



SEWGS :

$$CO + H_2O \leftrightharpoons CO_2 + H_2$$

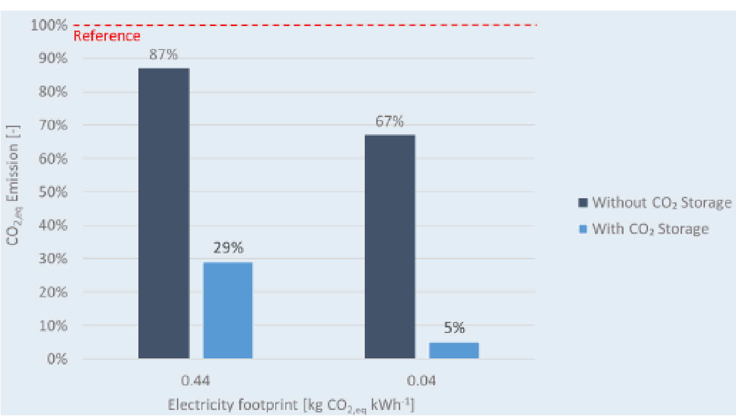
Ammonia production :

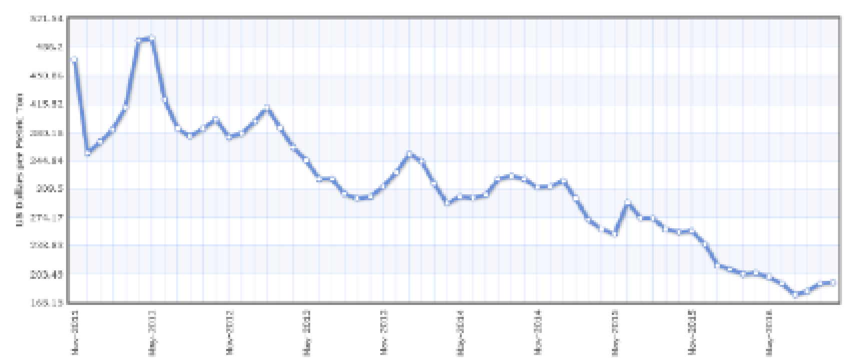
$$N_2 + 3H_2 \leftrightharpoons 2NH_3$$

Urea production :

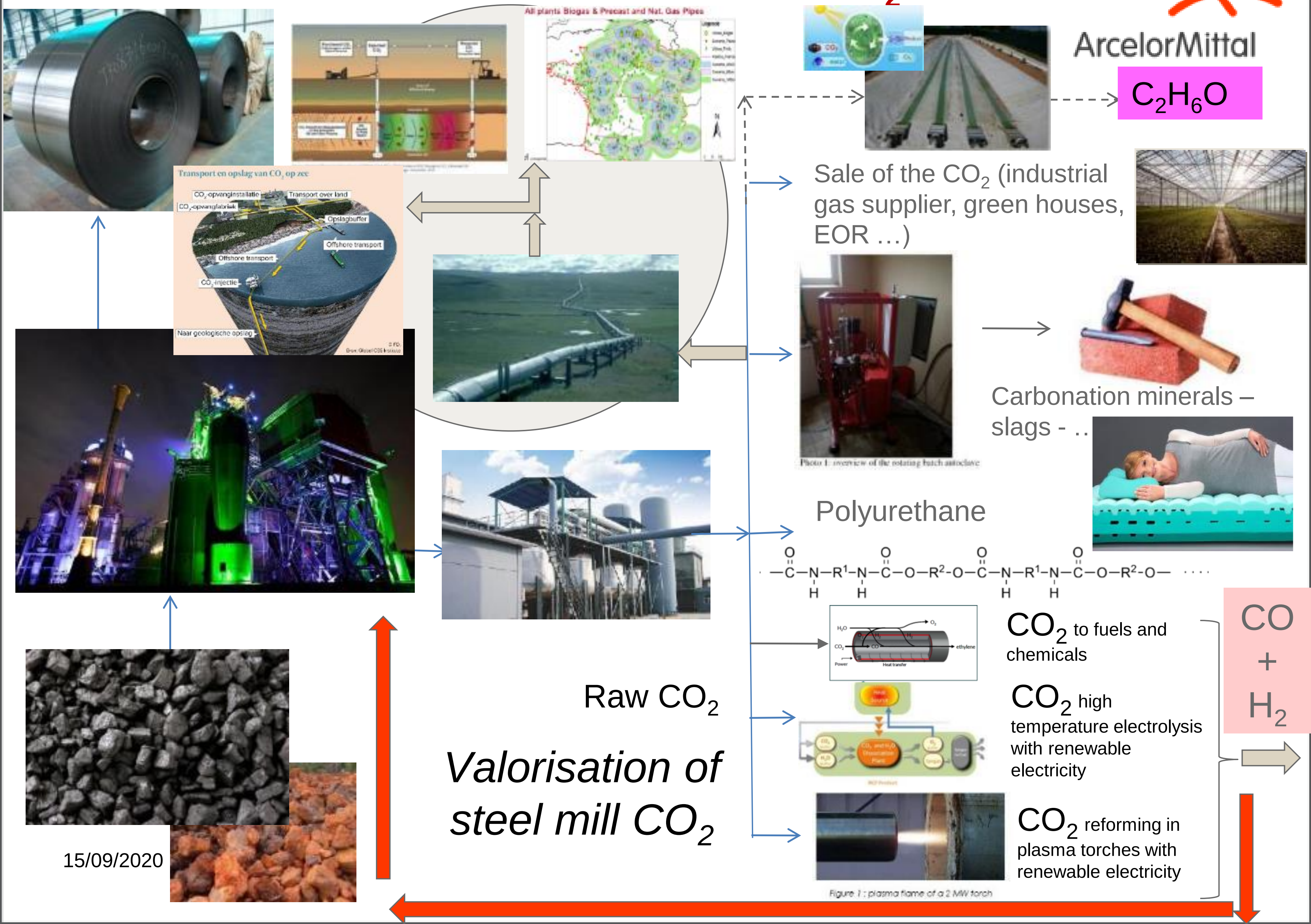
$$2NH_3 + CO_2 \leftrightharpoons NH_2COONH_4 \text{ (ammonium carbamate)}$$

$$NH_2COONH_4 \leftrightharpoons H_2O + NH_2CONH_2 \text{ (urea)}$$





The steel mill of the future …. will sell CO_2



The steel mill of the future …. will sell CO_2

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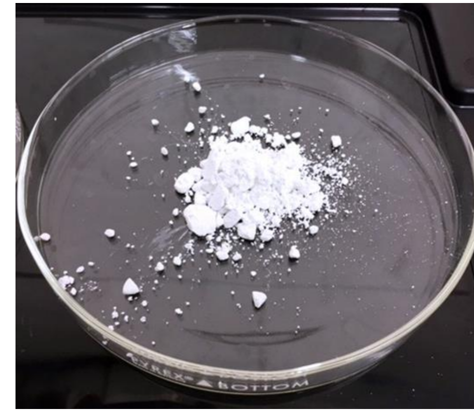
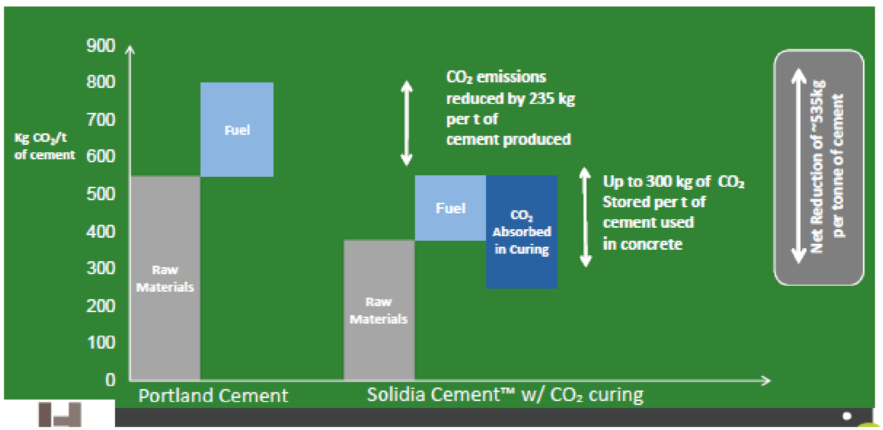
LafargeHolcim

PCC production



Up to 70% reduction in CO_2 footprint/t of cement used in concrete



CO2 VALORCO

Carbon8

CRH

RECOVAL

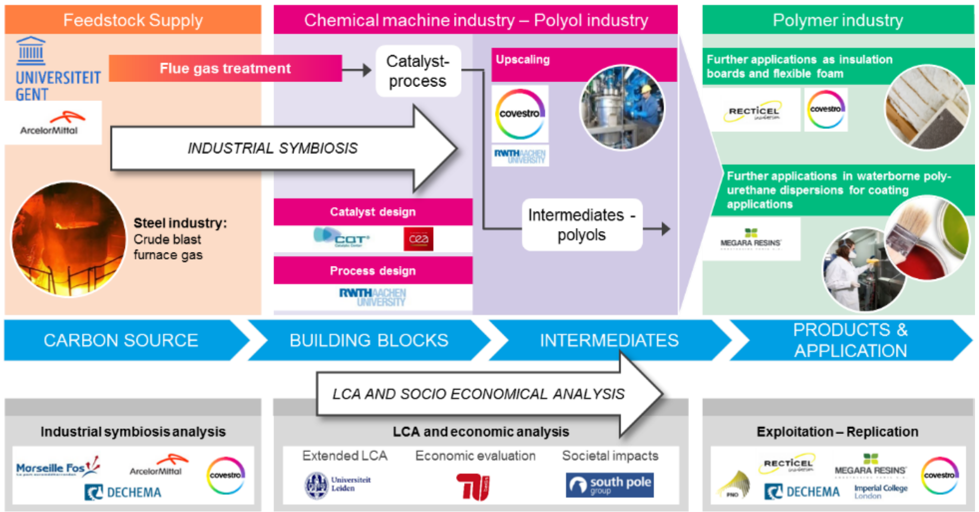
INDUSTRIAL PRODUCTION IN THE NETHERLANDS

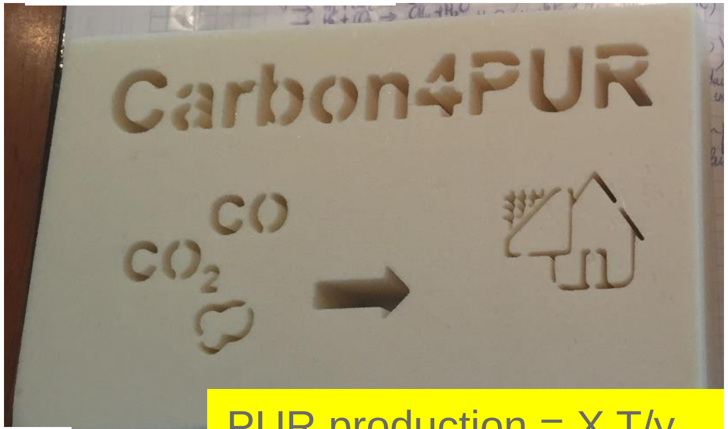
CO2Mpensatie steen

Carbon4PUR

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

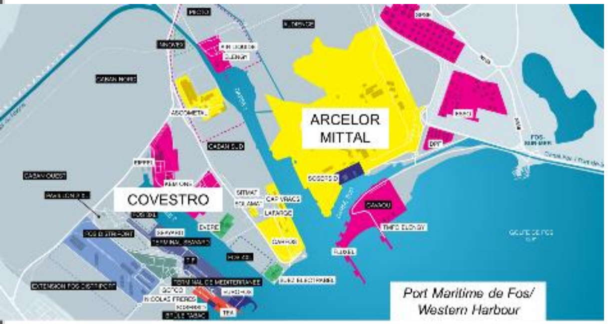
ArcelorMittal



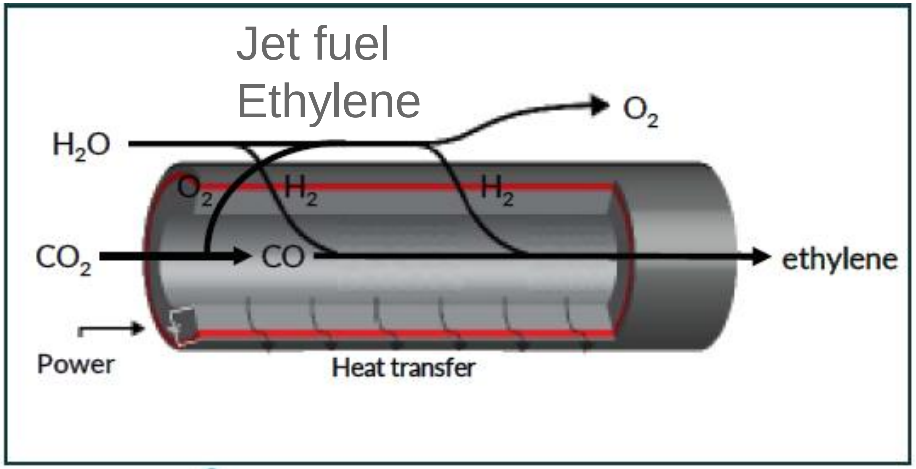


PUR production = X T/y
CO_2 avoided = 0,2 X T/y

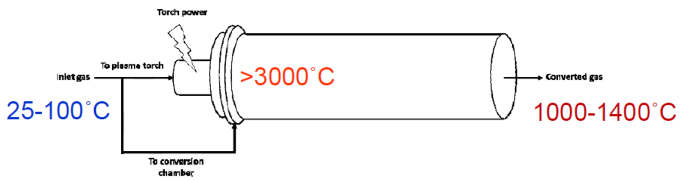
CCU



eCOCO2



IGAR project at AMAL Dunkirk



Agence de l'Environnement et de la Maîtrise de l'Energie

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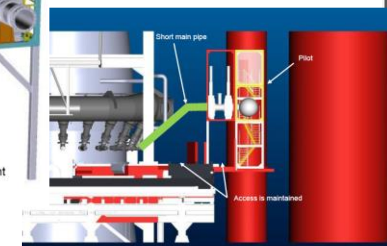
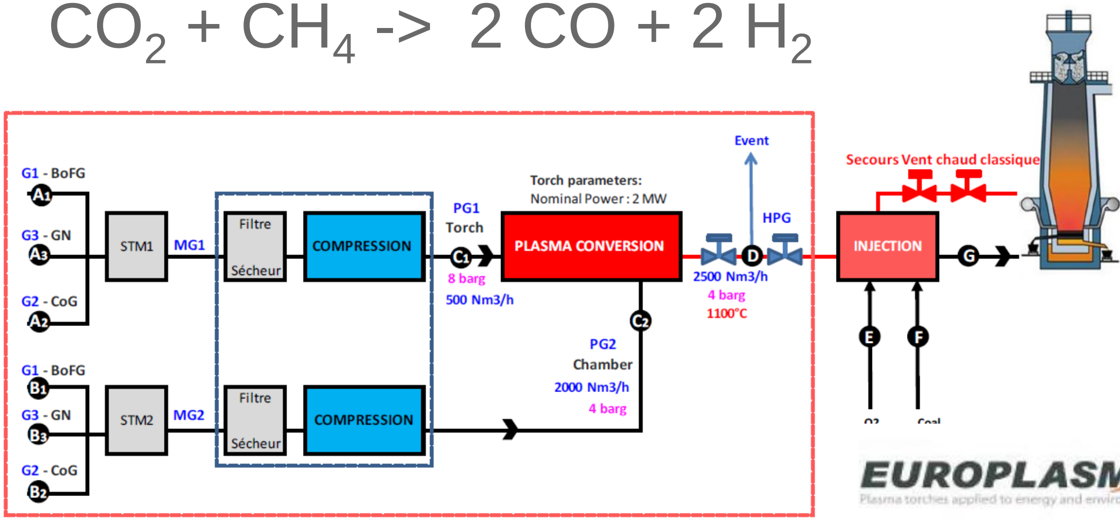


$$CO_2 + CH_4 \rightarrow 2\,CO + 2\,H_2$$



DK HF2 Situation – Outside view

2 connections (pipes to be installed)

EUROPLASMA
Plasma torches applied to energy and environment

Vasco2

Algae project at AM Fos sur Mer

15/09/2020

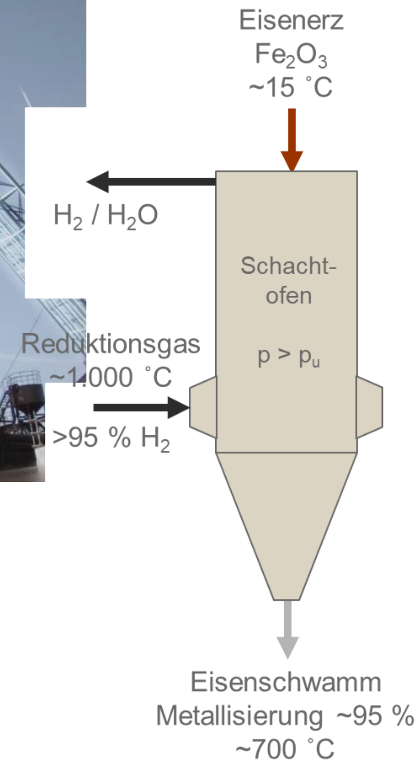
Photo 3 : Bassin 10 m² de culture de micro algues marines avec fumées industrielles – site Arcelormittal.

Agence de l'Environnement et de la Maîtrise de l'Energie

H_2 based steelmaking project at AM Hamburg

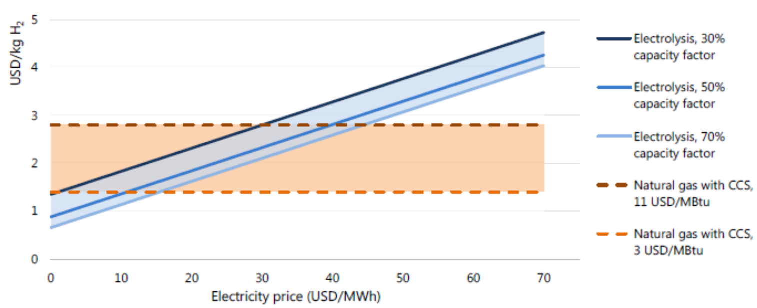
2019 Top 5 DRI Producing Nations

COUNTRY	PRODUCTION (Million Tons)
India	33.74
Iran	28.52
Russia	8.03
Mexico	5.97
Saudi Arabia	5.79



32

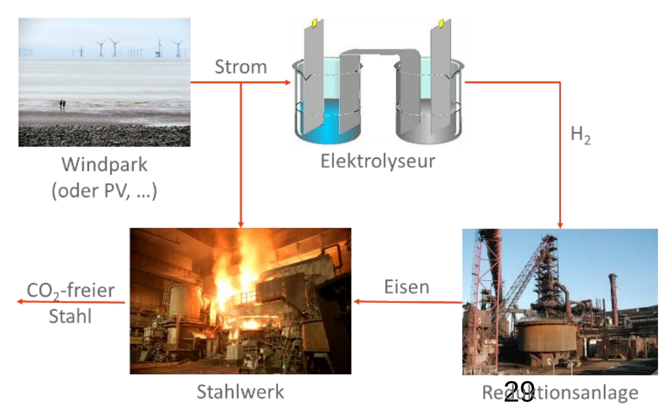
Figure 17. Comparison of hydrogen production costs from electricity and natural gas with CCS in the near term



Notes: CAPEX: electrolyser USD 700/kW$_e$, SMR w CCS USD 1 360/kWH$_2$; full load hours of hydrogen from natural gas 8 300 h; efficiencies (LHV): electrolyser 70%, gas with CCS 69%; capture rate for gas with CCS of 90%; discount rate: 8%.
Source: IEA (2019a), *The Future of Hydrogen: Seizing Today's Opportunities.*

Depending on local gas prices, electricity at USD 10/MWh to USD 40/MWh and at full load hours of around 4 000 h is needed for water electrolysis to become cost competitive with natural gas with CCUS.

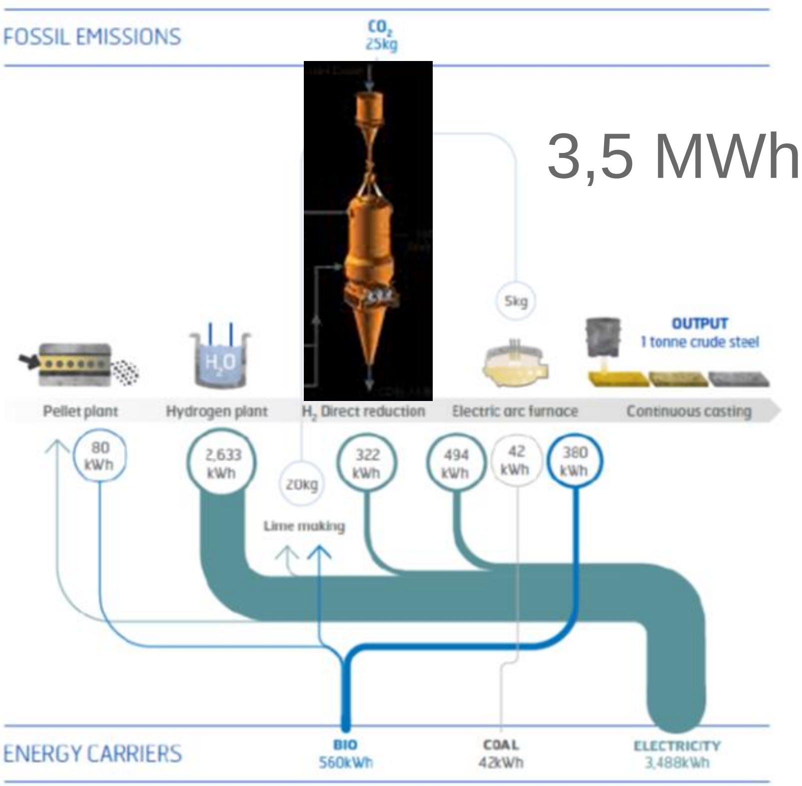
Vision für CO_2-freie Stahlerzeugung



AM is looking to the use of renewable electricity in different ways :

ArcelorMittal

Use of green hydrogen in DRI making :



3,5 MWh/t

Direct electrolysis of Fe :

3,11 MWh/t

The steel mill of the future …. may have a legal problem
… and no market for its products

ArcelorMittal

RED 2 : 2020 - 2030 Recycled Carbon Fuels

Many of these products will cost more than the fossil products

1. The LCA-methodology has to be defined and accepted in a delegated act. The minimum threshold of GHG reduction is not yet fixed (renewable electricity is privileged for transport = EV)

2. Member states can decide themselves if they allow Recycled Carbon Fuels in the energy mix for transport

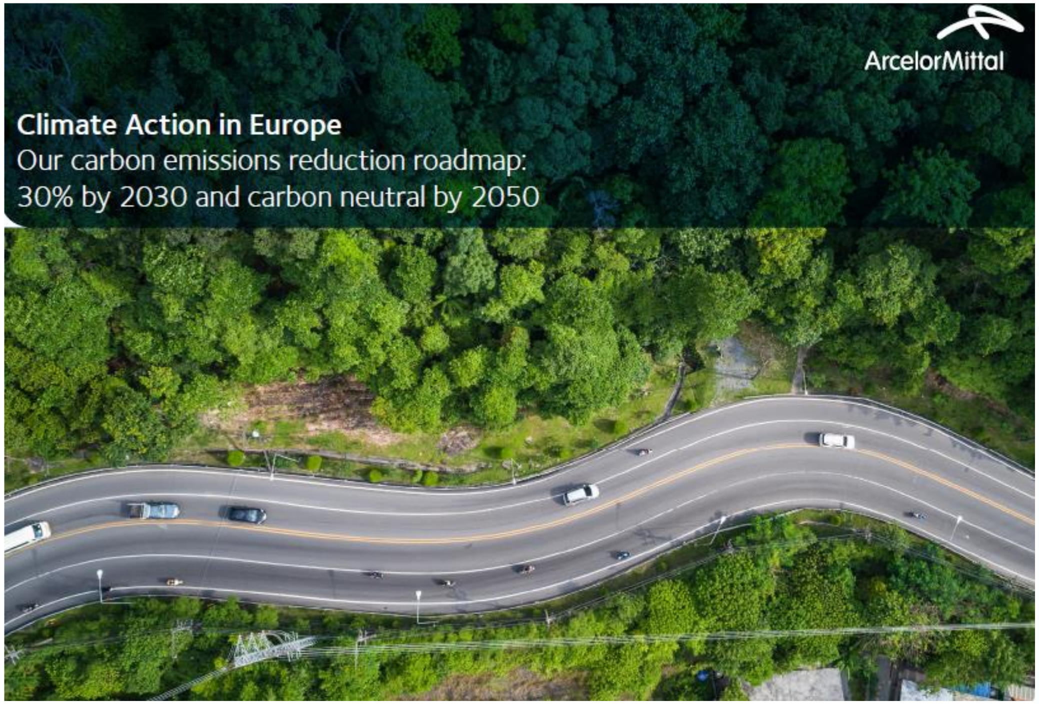
3. The CO_2 taxes for re-used carbon may not be eliminated (ETS)

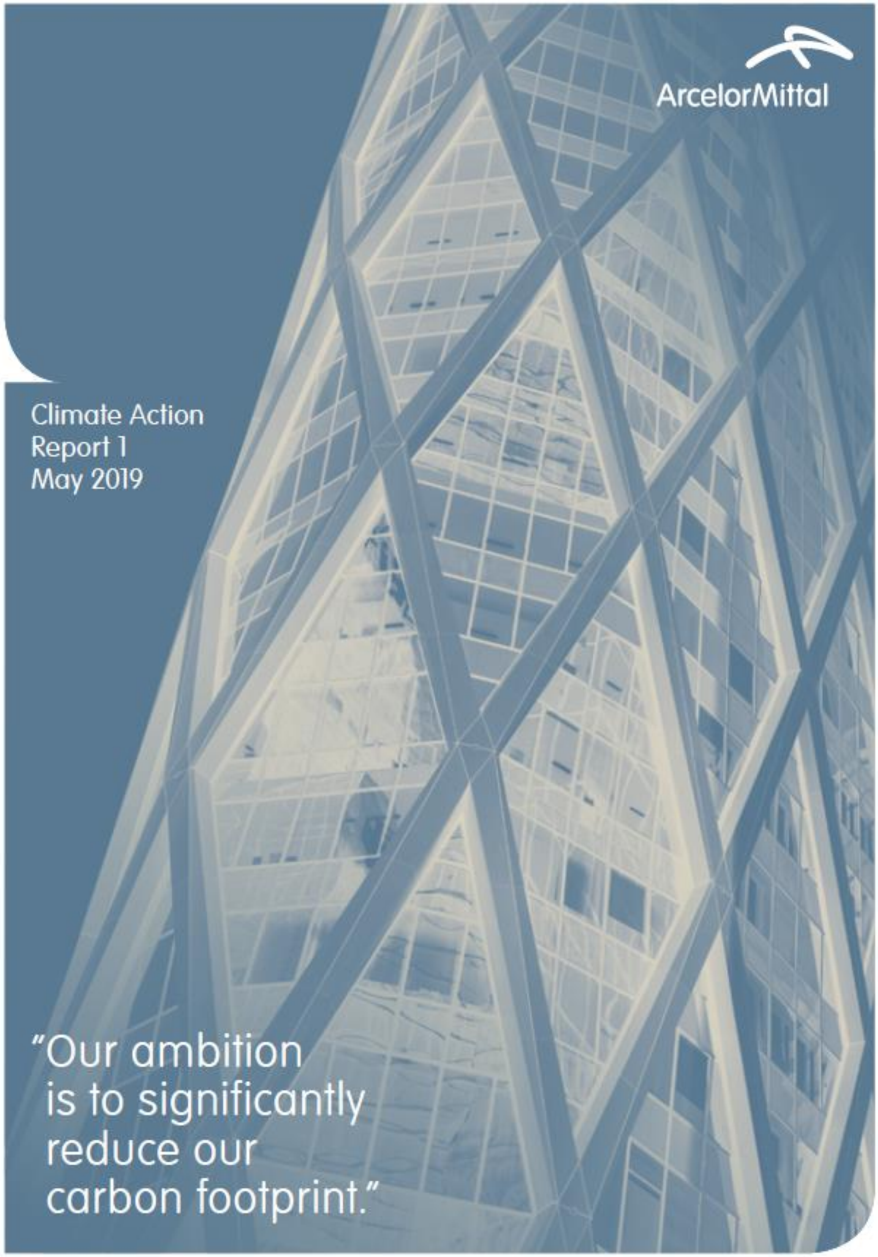
The promotion of recycled carbon fuels can also contribute towards the policy objectives of energy diversification and transport decarbonisation when they fulfil the appropriate minimum greenhouse gas savings threshold. It is therefore appropriate to include those fuels in the obligation on fuel suppliers, whilst giving Member States the option not to consider these fuels in the obligation if they do not wish to do so. Since those fuels are of non-renewable nature, they should not be counted towards the overall EU-target for energy from renewable sources.

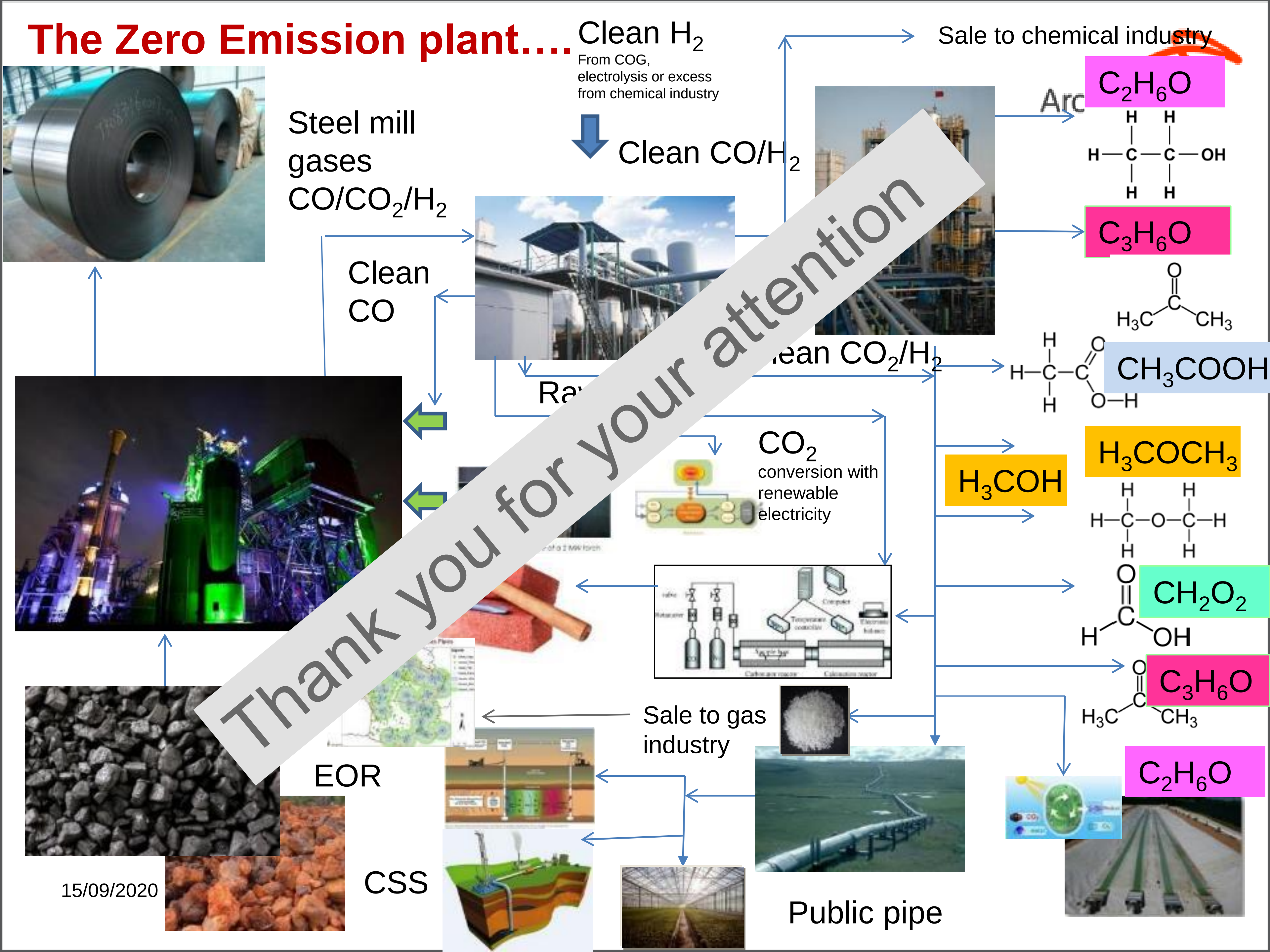
EUROPEAN COMMISSION

greenhouse gas emission savings from renewable liquid and gaseous transport fuels of non-biological origin and recycled carbon fuels, which shall ensure that no credit for avoided emissions be given for carbon dioxide whose capture already received an emission credit under other legal provisions.

https://www.worldsteel.org/media-centre/industry-member-news/2019-member-news/ArcelorMittal-publishes-first-Climate-Action-report.html






The Zero Emission plant….
Clean H_2
From COG, electrolysis or excess from chemical industry
Clean CO/H_2
Sale to chemical industry
Steel mill gases $CO/CO_2/H_2$
Clean CO
Clean CO_2/H_2
C_2H_6O
C_3H_6O
CH_3COOH
H_3COCH_3
H_3COH
CH_2O_2
C_3H_6O
C_2H_6O
CO_2
conversion with renewable electricity
Sale to gas industry
EOR
CSS
Public pipe
Thank you for your attention
15/09/2020

INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILIZATION

TU/E - EINDHOVEN - 16-17 FEBRUARY 2021

Session 1A (chairperson Josè Luis Viviente)	
11:15-11:35	Dr. O. David - A review of the membrane development steps from material to final product
11:35-11:55	Dr. V. Spallina - System simulation for integration of CO_2 capture technologies into steelworks and CCUS clusters
11:55-12:15	Dr. M. Saric - Methanol membrane reactor: modelling and experimental results
12:15-12:35	Dr. Adam Deacon - Realising the potential of MOFs through efficient scale-up
12:35-12:55	Dr. M. Etxeberria-Benavides - PBI based mixed matrix hollow fiber membranes for pre-combustion CO_2 capture

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WE
CAN DO
SO MUCH
TOGETHER

INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILIZATION
TU/E - EINDHOVEN - 16-17 FEBRUARY 2021

Membrane development steps: from material to final product

Dr Oana David

tecnalia Inspiring Business

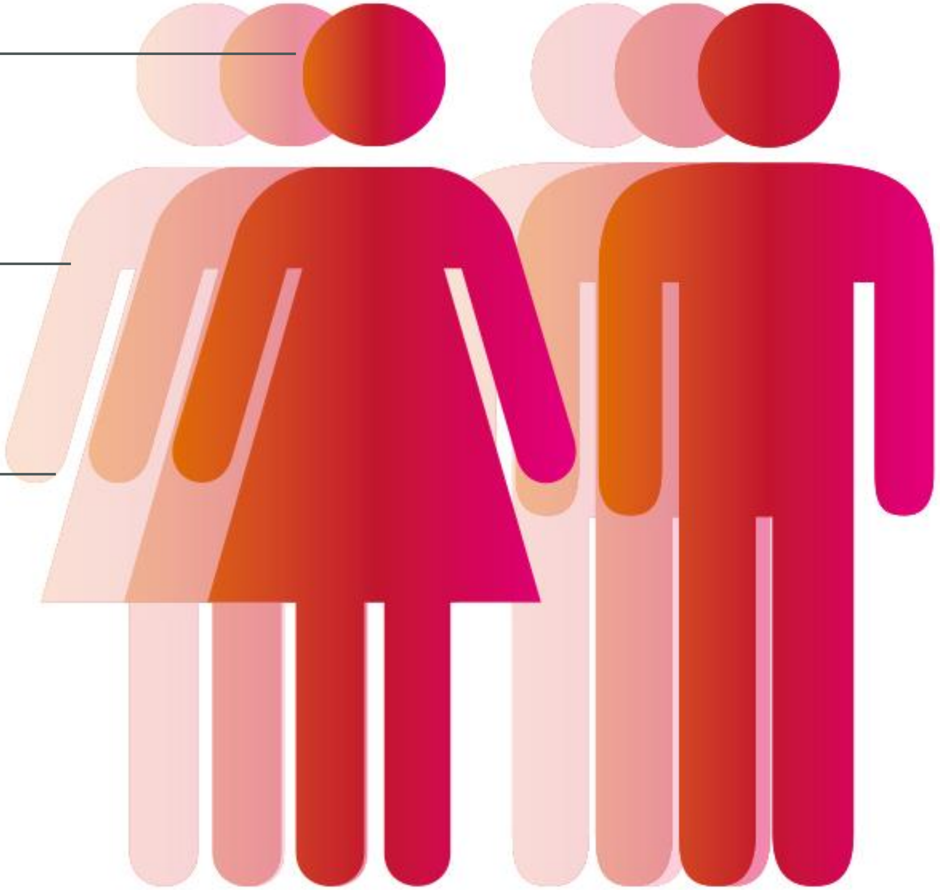
DSS2016.EU DSSINNOVA 2016

FUNDACION TECNALIA RESEARCH & INNOVATION

is a private non profit research centre.

Main figures
in 2017

PEOPLE
IN TECNALIA



1,445 STAFF

57 % MEN

43 % WOMEN

27 DIFFERENT NATIONALITIES

43 AVERAGE AGE

249 NUMBER OF PHDS

Figures on 31 December 2017.

BALANCE OF ACTIVITIES AND FUNDING

FIGURES ON
31 DECEMBER 2017

INCOME

104 MILLION EUROS

47,1%

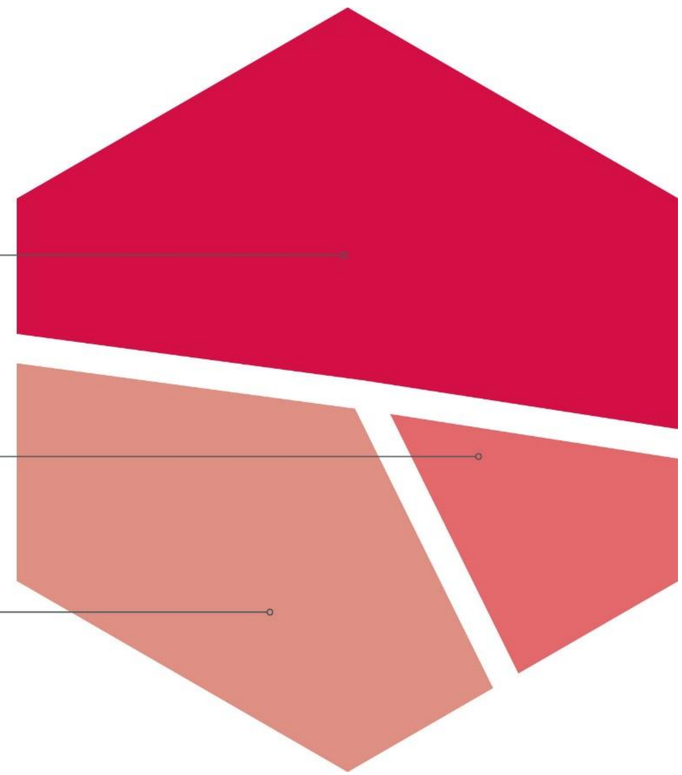
PRIVATE FINANCING AND OTHERS

19,7%

NON-COMPETITIVE PUBLIC FUNDING

33,2%

COMPETITIVE PUBLIC FUNDING



FUNDACION TECNALIA RESEARCH & INNOVATION

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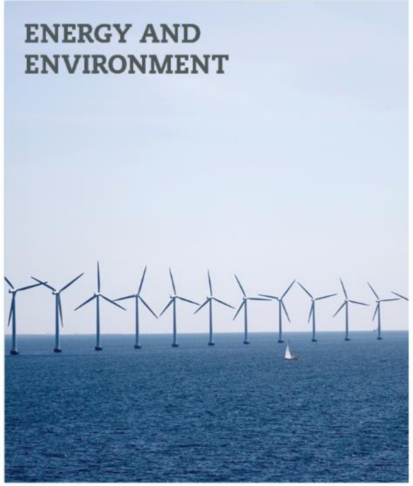
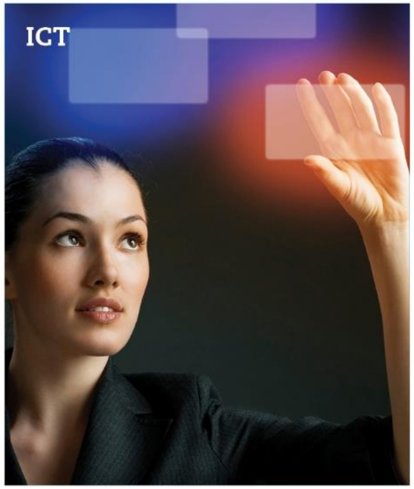
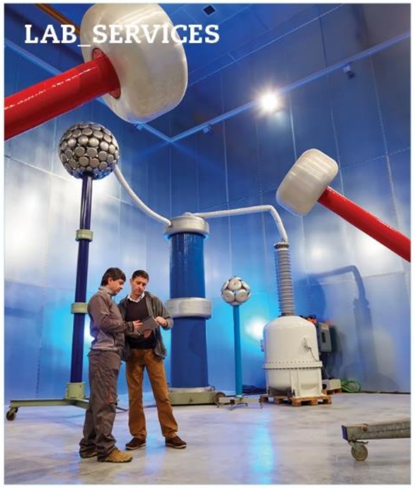
6 INTERCONNECTED
BUSINESS DIVISIONS

+ EMERGING BUSINESSES



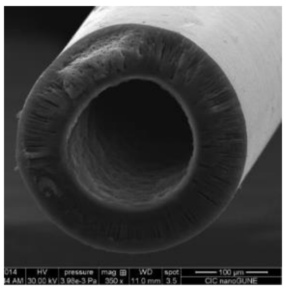


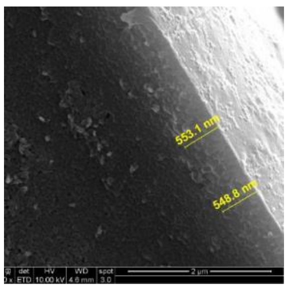


Membrane Technology and Process Intensification research group at TECNALIA

tecnalia Inspiring Business

Polymeric and Mixed matrix membranes	Carbon molecular sieve	Palladium membranes
Combination of polymer matrix with inorganic fillers: MOFs, zeolites,…	Pyrolized polymers. Unique pore structure	Thin Pd supported membranes. High H2 permeability & selectivity





Applications

- CO_2 Pre-combustion (H_2/CO_2)
- CO_2 Post-combustion (N_2/CO_2)
- Biogas upgrading (CO_2/CH_4)
- Natural gas upgrading (CO_2/CH_4)

Applications

- CO_2 Pre-combustion (H_2/CO_2)
- Biogas upgrading (CO_2/CH_4)

Applications

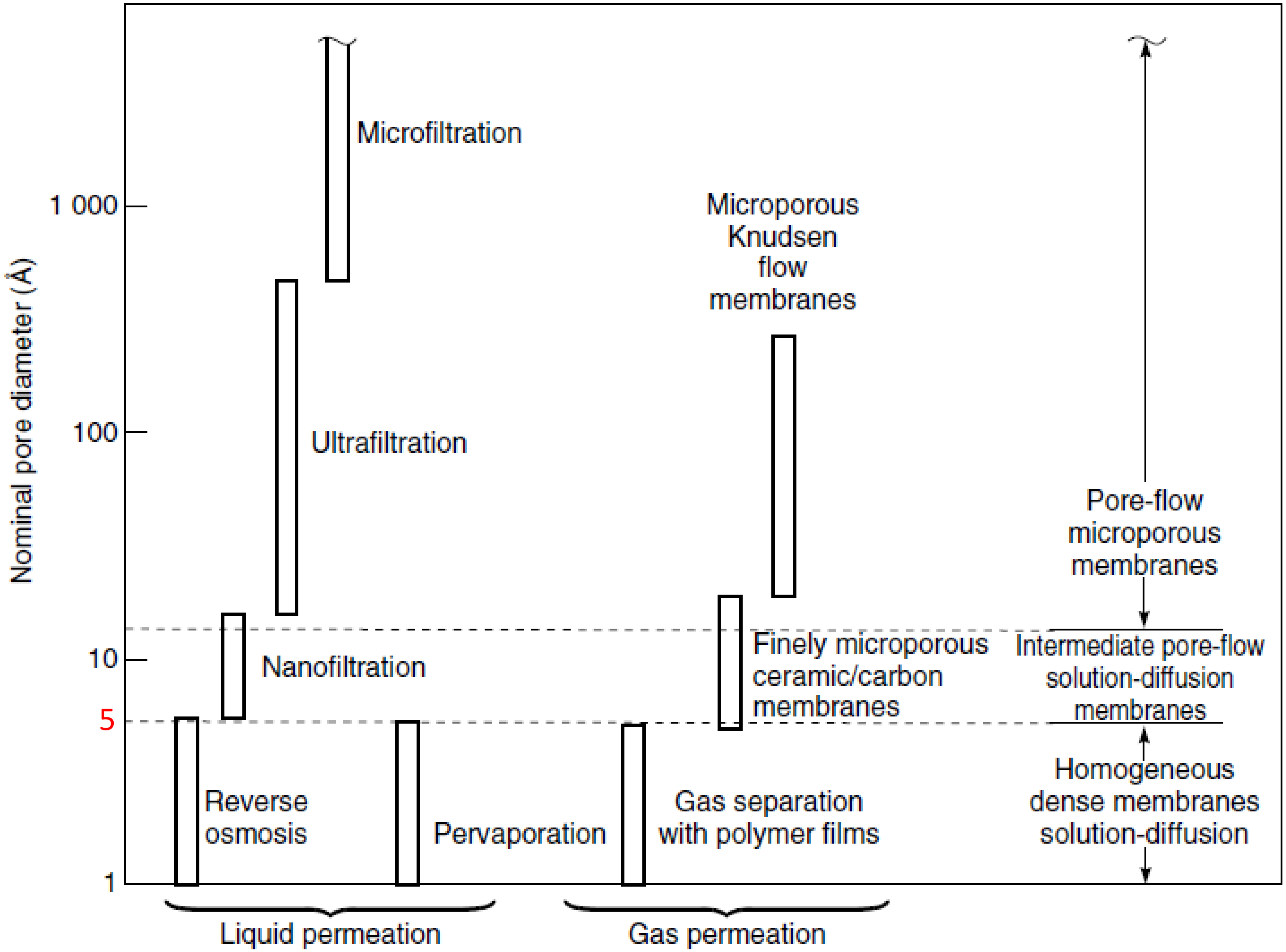
- CO_2 Pre-combustion (H_2/CO_2) & pure H_2 production

Membrane development steps:
from material to final product

Outlook:

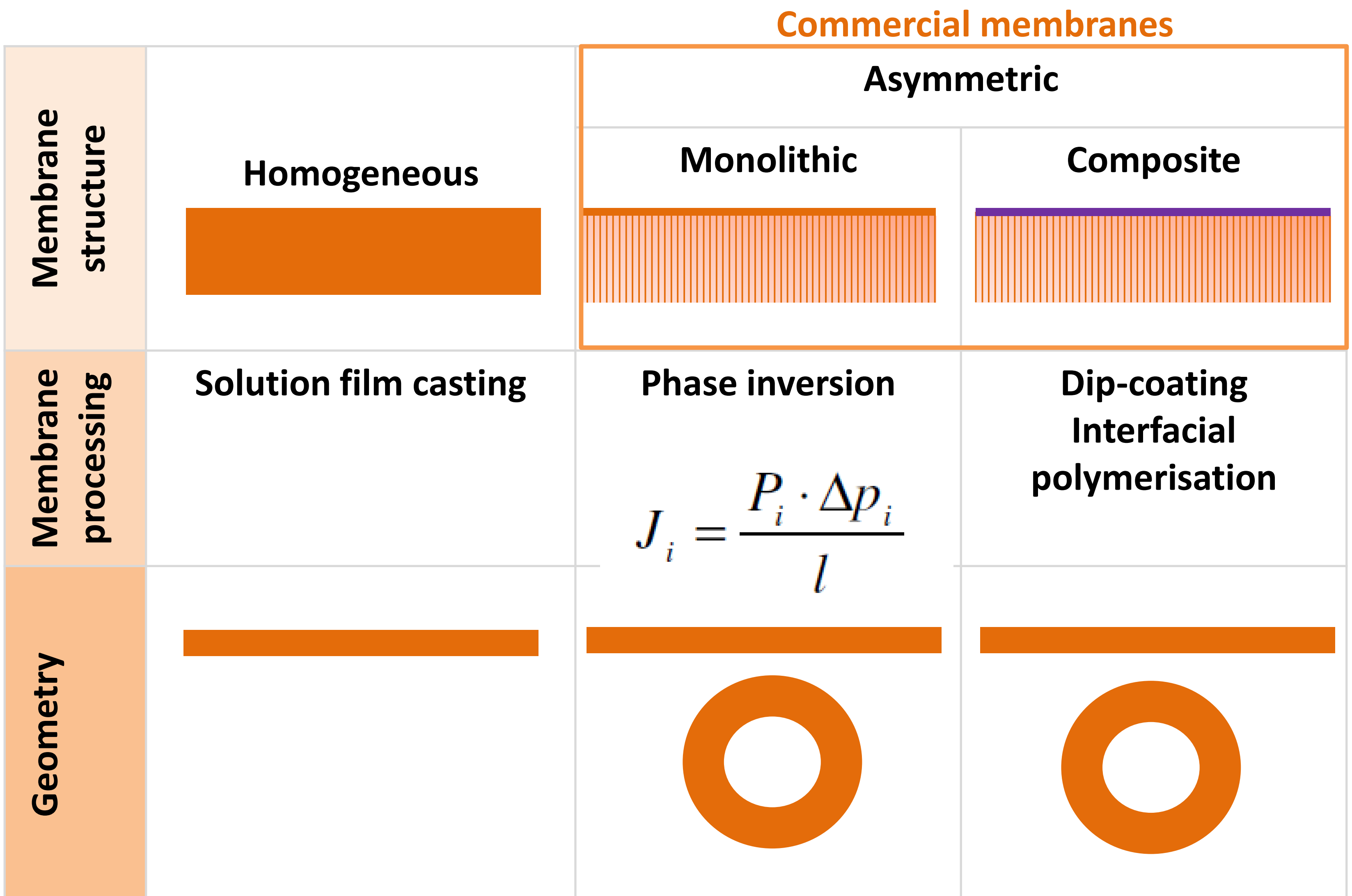
- ✓ Introduction to membrane processes
- ✓ Membrane structure and geometry for gas separation
- ✓ Membrane Development Strategy
- ✓ Applications and Tecnalia examples

Separation with membranes



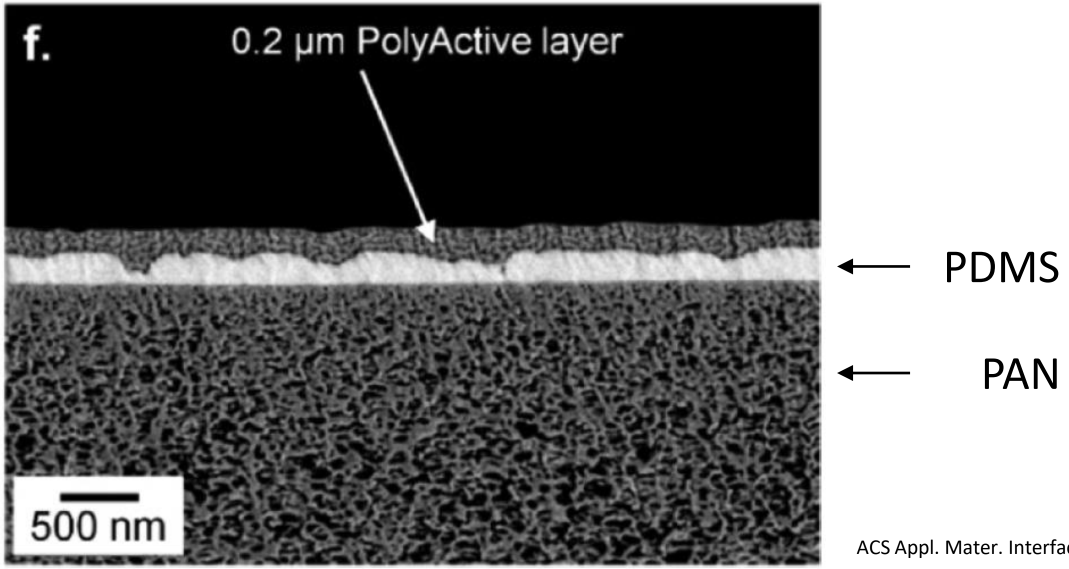
MEMBRANE STRUCTURE AND GEOMETRY

tecnalia Inspiring Business

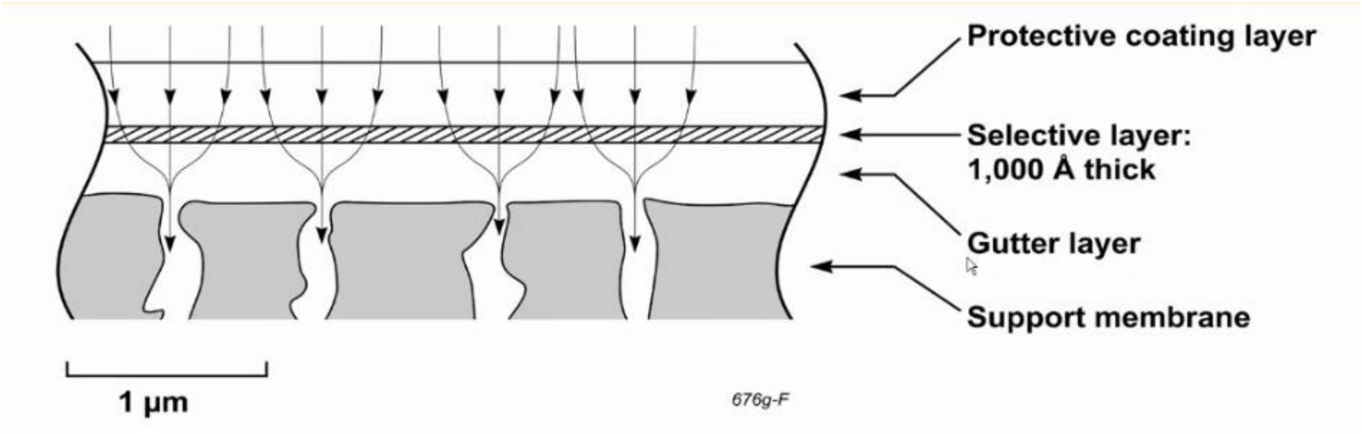


MEMBRANE STRUCTURE AND GEOMETRY

TFM: Thin film composite membrane



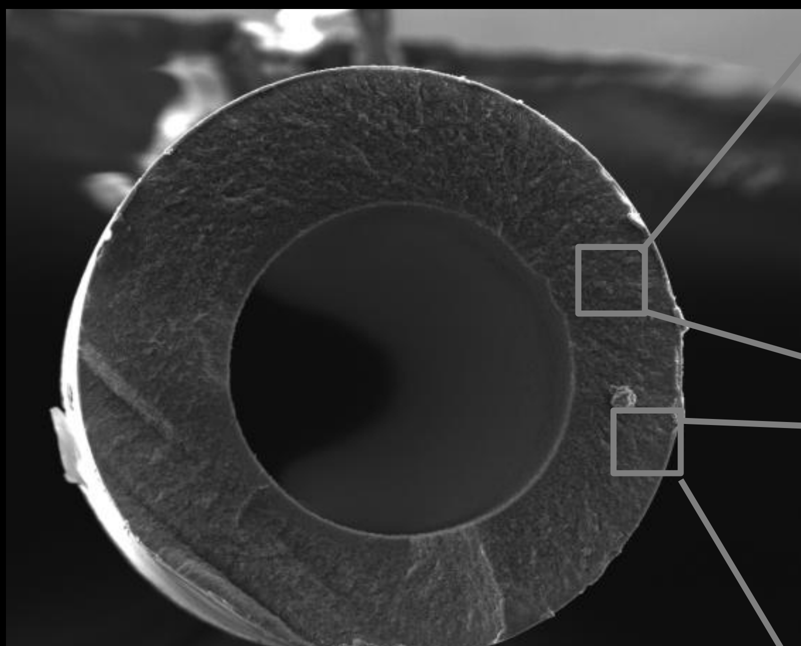
ACS Appl. Mater. Interfaces 2018, 10, 26733−26744



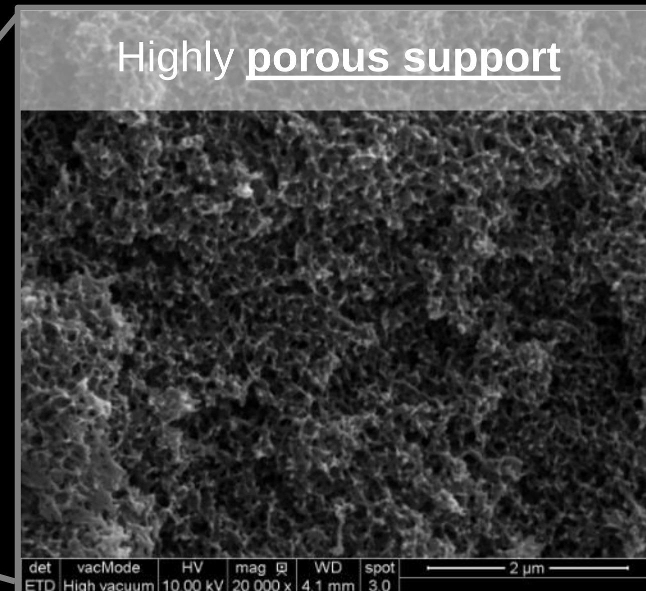
H. Linetal./JournalofMembraneScience457(2014)149–161

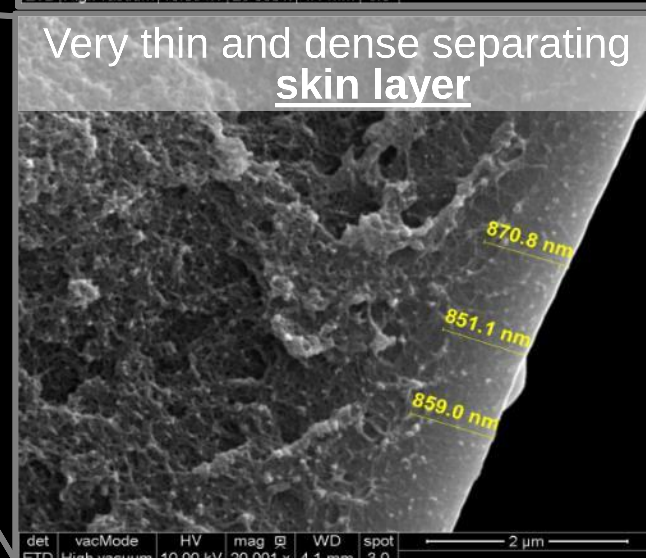
MEMBRANE STRUCTURE AND GEOMETRY

Monolithic hollow fiber membrane



Asymmetric hollow fiber

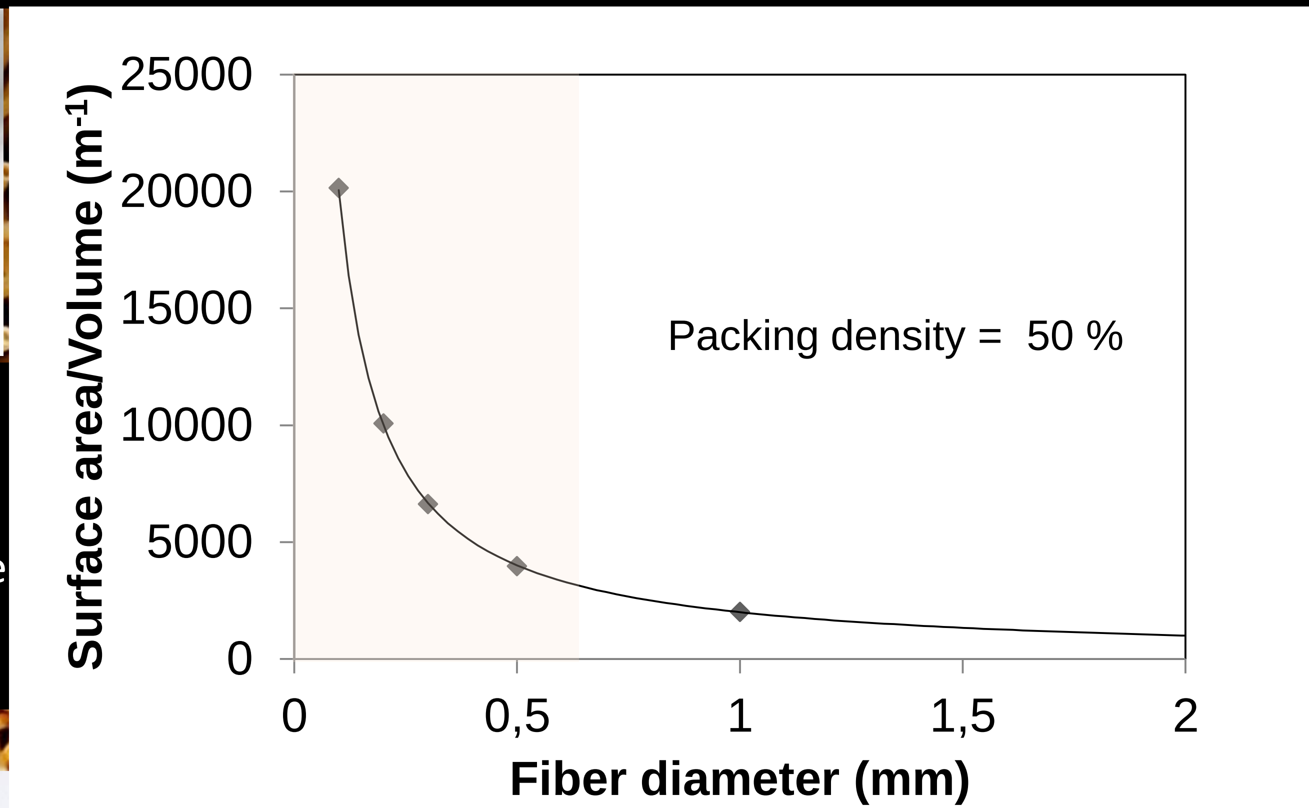




PRODUCTIVITY -

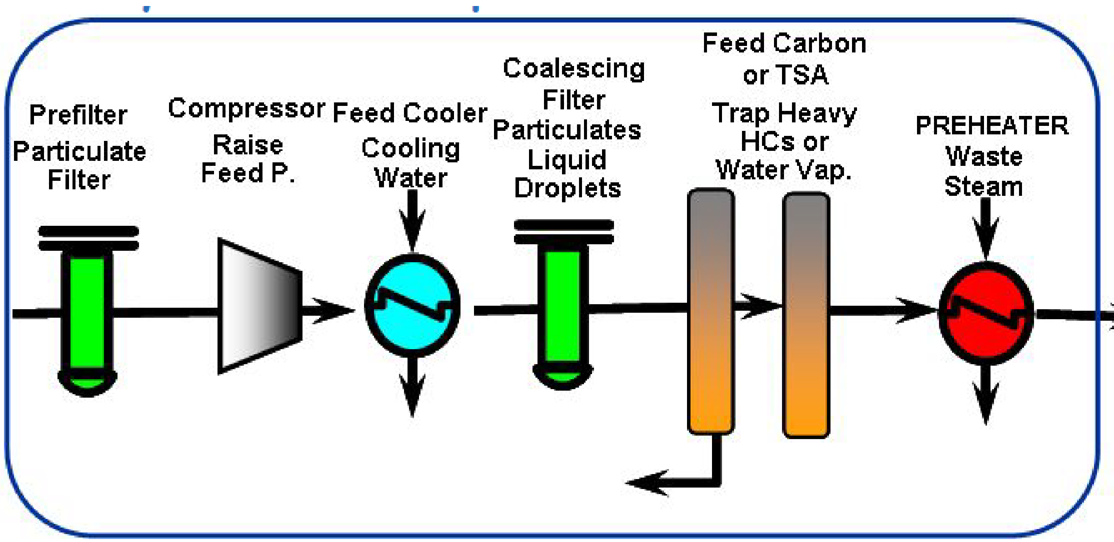
MEMBRANE GEOMETRY

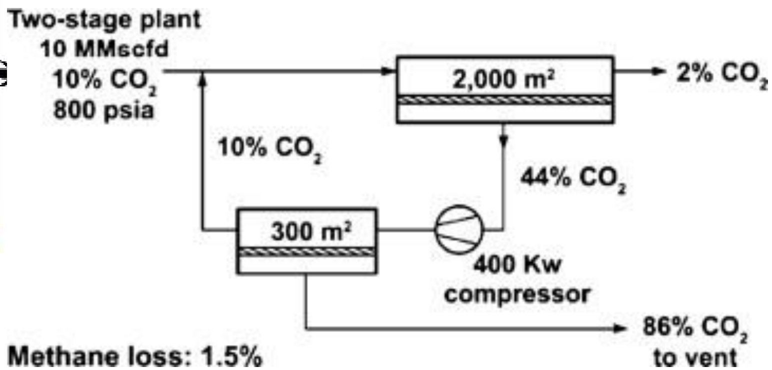
Perme



Process design and membrane system components

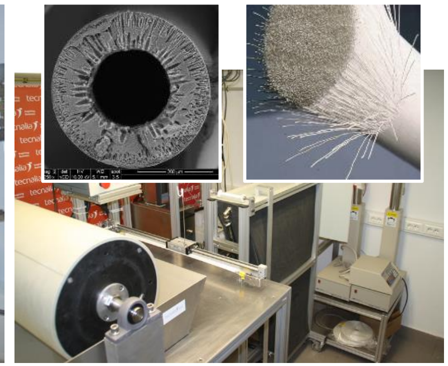
Natural gas treatment: CH4/CO2





R.W. Baker, K. Lokhandwala **Natural gas processing with membranes: an overview** Ind Eng Chem Res, 47 (2008), pp. 2109-2121

Membrane Development Strategy

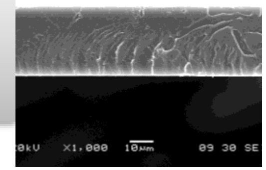
Process analysys and optimization	Membrane development	Membrane scale up and prototype construction	Membrane characterization
			
Analysis of the process (feed stream and desired performance) to propose the best performing possibilities.	Development/tuning up advanced membranes based on novel materials (Mixed Matrix, CMS or metallic membranes) to enhance the performance of the separation.	Production and integration into a prototype of different types of membranes.	Testing commercially available or internally developed membranes at different conditions that reproduce industrial requirements

Membrane Development Strategy

Defining target performance

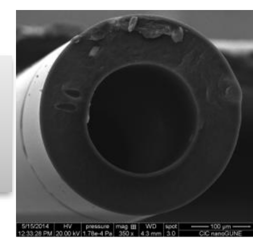
Material development and/or selection

Dense film preparation and characterization



Intrinsic separation properties
Permeability and selectivity

Hollow fiber preparation and characterization



Separation properties
Permeance and selectivity

Possible to Scale-up, Prototype??

Post-combustion CO_2 capture

Industrial requirements

- 4-20% CO_2 ingas from power generator
  - Low/Atmospheric pressure
  - Vapour, O_2, SO_x, NO_x, NH_3, …
  - High flows 40,000 Nm^3/h
- To be competitive with amine or 90% CO_2 capture for installed prices not less than 50 €/m^2

Specifications	Value	Unit
P_{CO2}	>2,250	GPU
CO_2/N_2 selectivity	>30	---
Temperature	100	ºC
Design pressure	7	bar
Costs	< 100*	€/m^2

*Target set by the BioCoMem project

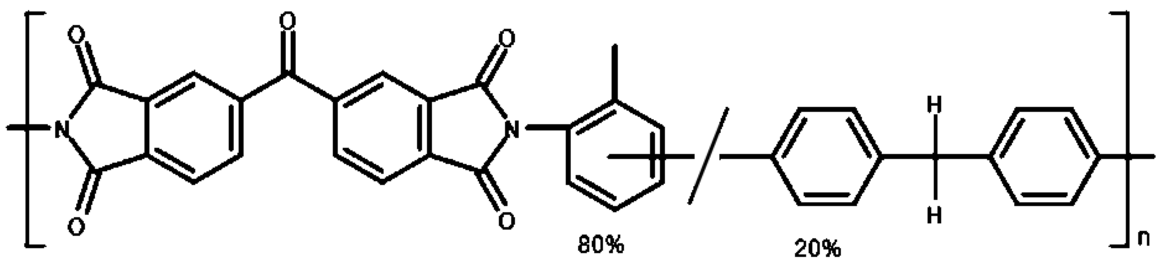
Haibo Zhai (2019)

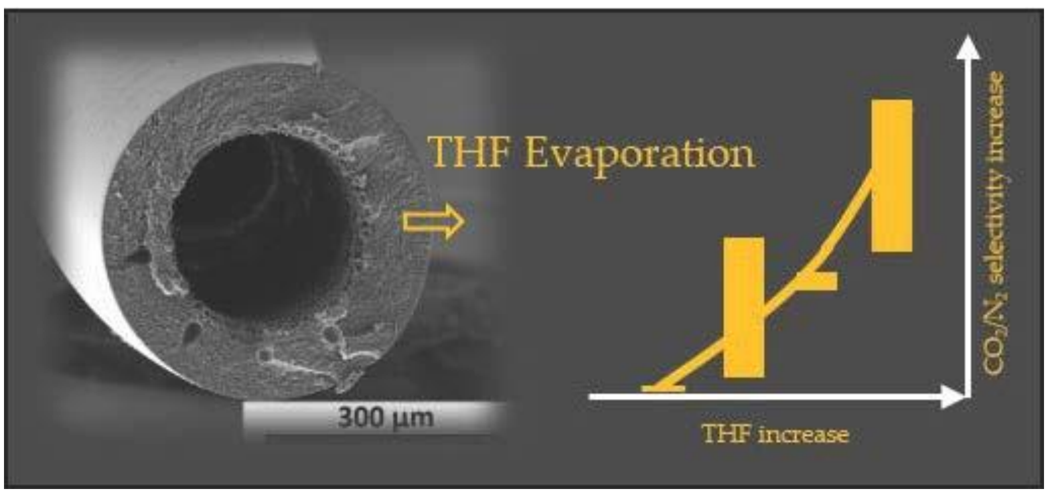
Polymer	P_{CO2} (Barrer)	Selectivity CO_2/N_2	Selectivity CO_2/CH_4	Test conditions	Ref.
PEBAX 1657 (60PEO/PA6)	79	52,7	16,8	30 ºC	1
PEBAX 1074 (55PEO/PA12)	110,67	51,4	11,09	25 ºC	2
PEBAX 2533 (80PTMEO/PA12)	149	15	7,28	25 ºC	3
Polyactive	202	44	15,2	35 ºC	4
PE (Alathon 14)	12,6	13	-	-	5
6FDA-DAM	842,41	15,3	18	T = 35ºC/ p = 100PSI	6
PPO	75,8	19,9	6,89	Tª: 30ºC	7
Matrimid	7	25	33,33	Tª: 35ºC p: 3,5 bar	8
Cellulose Acetate	6,3	30	30	Tª: 30ºC p: nd	7
Polysulfone	5,6	22,4	22,4	Tª: 30ºC p: nd	7
Polietersulfone (Radel A)	2,51	30,61	29,9	Tª: 35ºC p: 10 atm	9
Polyeterimide (Ultem)	1,32	28,09	37,71	Tª: 30ºC p: nd	7
P84	0,99	40,20	>40	Tª: 25ºC	10

1. JMS 467(2014)269–278
2. Chemical Engineering Research and Design 117 (2017) 177-189
3. Silicon 10, 1461–1467 (2018)
4. JMS 535 (2017) 350-356
5. Bixler, H. J.; Sweeting, O. J. In Science and Technology of Polymer Films; Sweeting, O. J., Ed.; Wiley-Interscience: New York, 1971; pp 1–130.
6. Polymer 54 (2013) 6226-6235
7. Abetz, V., et all Adv. Eng. Mater., 8 (2006) 328-358.
8. Polymer 49 (2008) 1594
9. JMS 277 (2006) 28-37
10. JMS 216 (2003) 195-205

Post-combustion CO_2 capture

P84 Asymmetric hollow fiber membranes



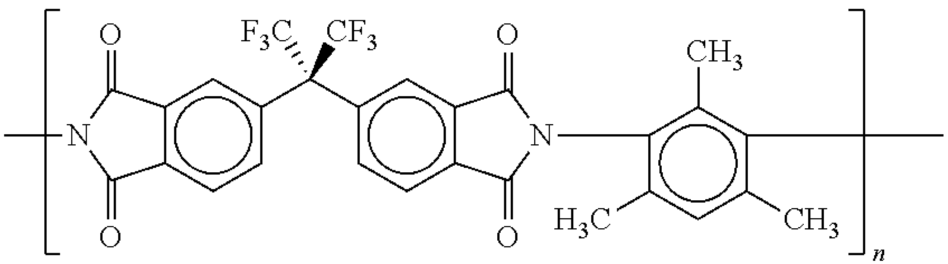


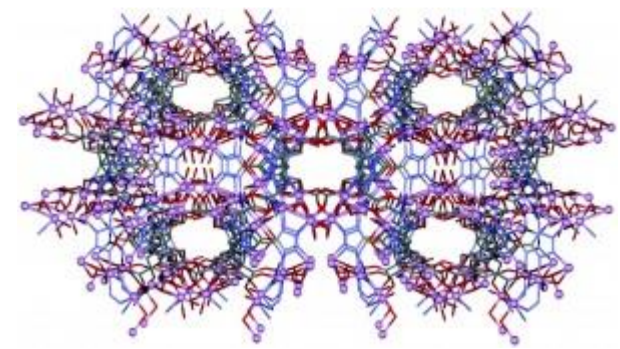
- highly thin (~56 nm) defect-free skin
- CO_2/N_2 selectivity of 40, and a CO_2 permeance of 23 GPU at 35 °C
- No post treatment necessary for post treatment
- Scaled up the process at 5000 m fiber with reproducible results

Etxeberria-Benavides, M.; Karvan, O.; Kapteijn, F.; Gascon, J.; David, O. Fabrication of Defect-Free P84® Polyimide Hollow Fiber for Gas Separation: Pathway to Formation of Optimized Structure. Membranes 2020, 10, 4.

Post-combustion CO_2 capture

MMM flat sheet ZIF-94 Filler and 6FDA-DAM Polymer



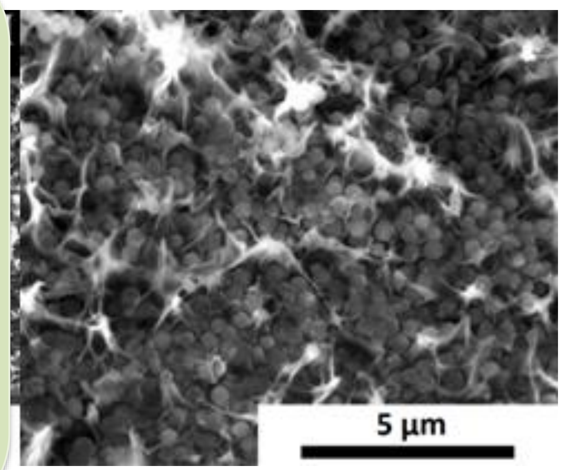


Mixed Matrix Membranes

Filler (Molecular sieve)
+
Matrix (Polymer)

- Mechanical stability
- Easy processing

- Chemical stability
- Gas sieving properties

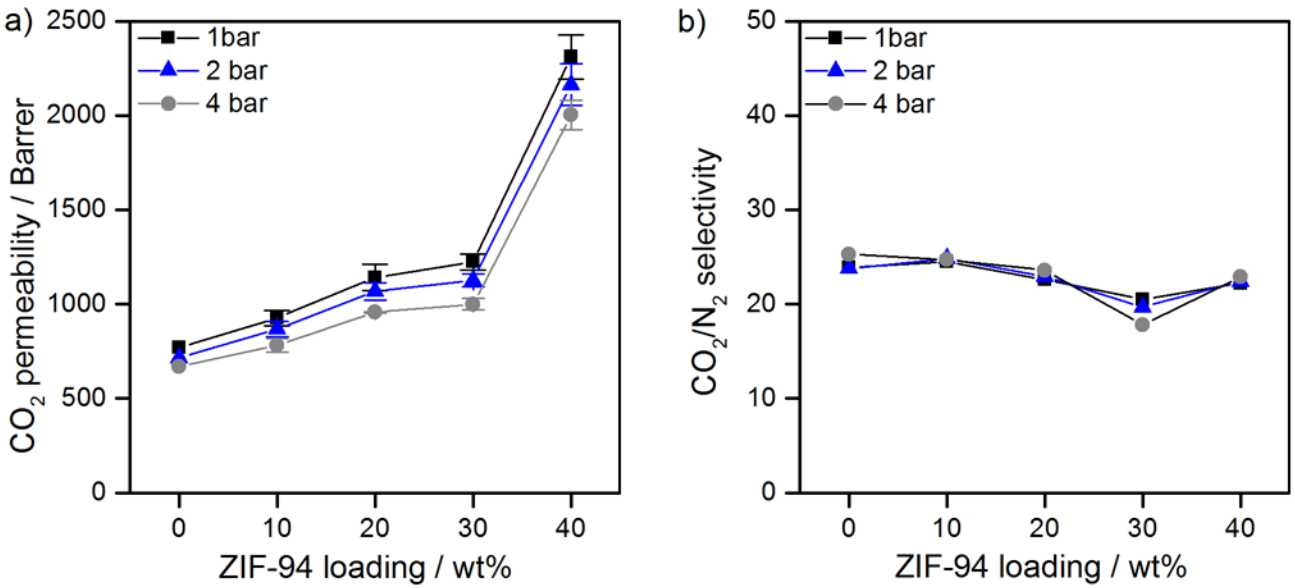


Miren Etxeberria-Benavides, Oana David, Timothy Johnson, Magdalena M. Łozińska, Angelica Orsi, Paul A. Wright, Stefan Mastel, Rainer Hillenbrand, Freek Kapteijn, Jorge Gascon, High performance mixed matrix membranes (MMMs) composed of ZIF-94 filler and 6FDA-DAM polymer, Journal of Membrane Science, Volume 550, 2018, Pages 198-207

Post-combustion CO_2 capture

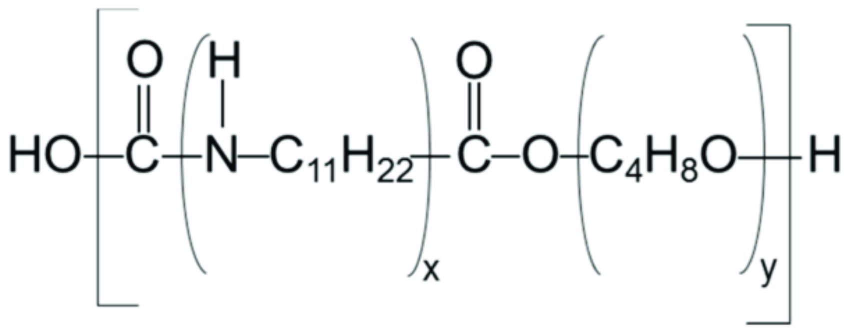
MMM flat sheet ZIF-94 Filler and 6FDA-DAM Polymer

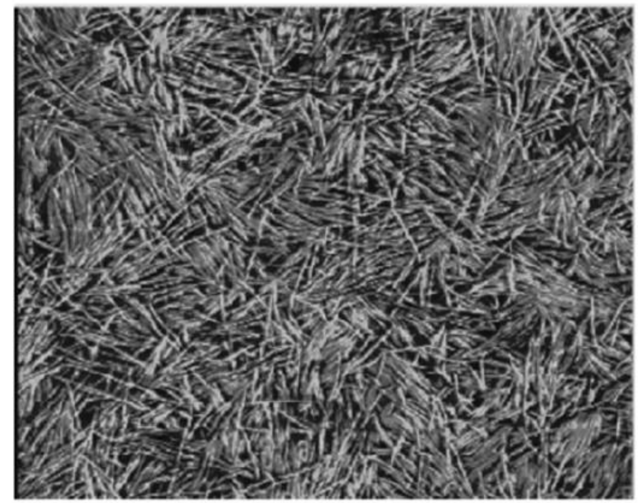
Mixed Gas CO_2/N_2 = 15/85



Post-combustion CO_2 capture

Bio based PEBAX co-polymers





Polymer	P_{CO2} (Barrer)	Selectivity CO_2/N_2	Selectivity CO_2/CH_4	Test conditions	Ref.
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PEBAX 1074 (55PEO/PA12)	111	51,4	11,09	25 ºC	2
PEBAX 2533 (80PTMEO/PA12)	149	15	7,28	25 ºC	3
Polyactive	202	44	15,2	35 ºC	4
Bio-PEBA	**320**	**46,6**	**14,2**	**35 ºC**	**Biocomem**

www.biocomem.eu

Thank you for your attention

Questions

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http://blogs.tecnalia.com/inspiring-blog/

www.tecnalia.com

System simulation for integration of CO_2 capture technologies into steelworks and CCUS clusters

Vincenzo Spallina[1], Sergey Martynov[2], Richard Porter[2], Haroun Mahgerefteh[2]

[1]Department of Chemical Engineering and Analytical Science, University of Manchester
[2]Department of Chemical Engineering, University College London

email: vincenzo.spallina@manchester.ac.uk

International Workshop on CO_2 Capture and Utilization
16-17 February 2021

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884418

C4U

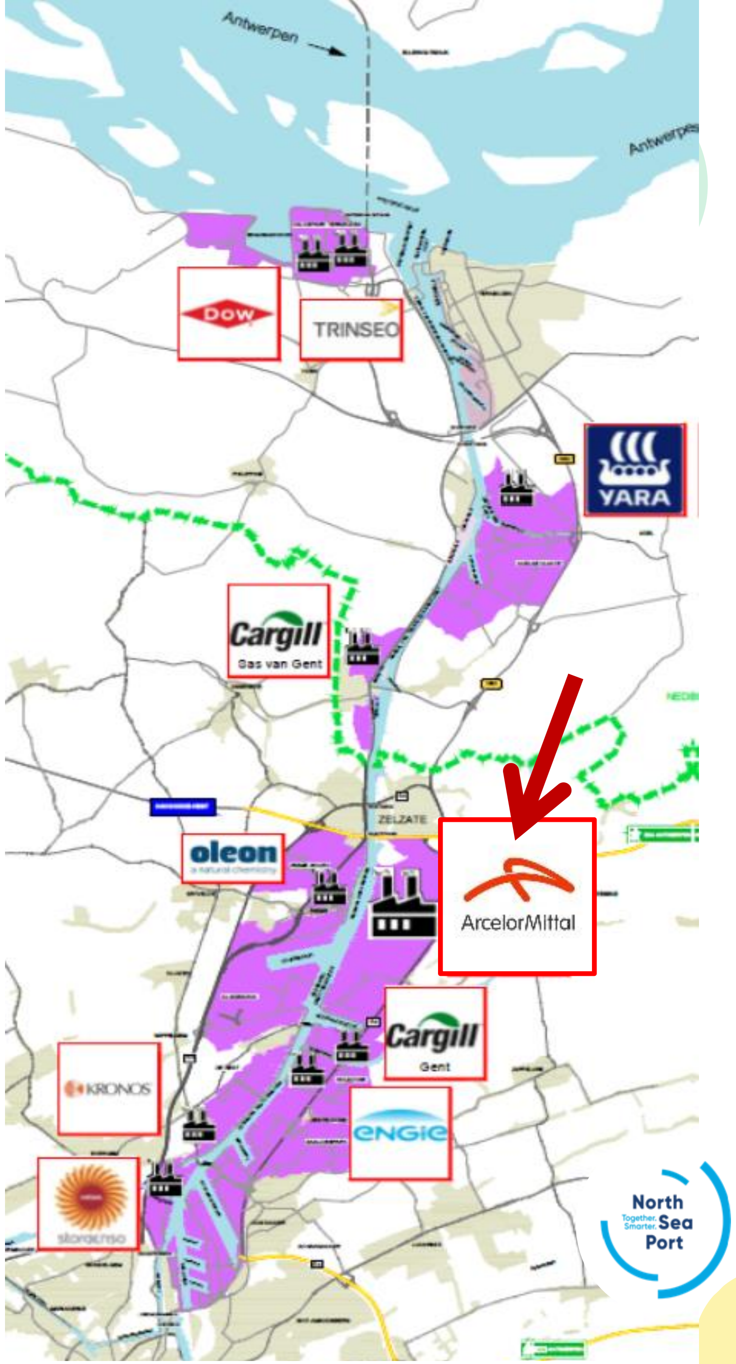
Advanced Carbon Capture for Steel Industries Integrated in CCUS Clusters

Start date:	1 April 2020
End date:	31 March 2024
Overall budget:	€ 13,845,496
Coordinator:	Prof. Haroun Mahgerefteh, University College London

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884418

C⁴U: Headline Objectives

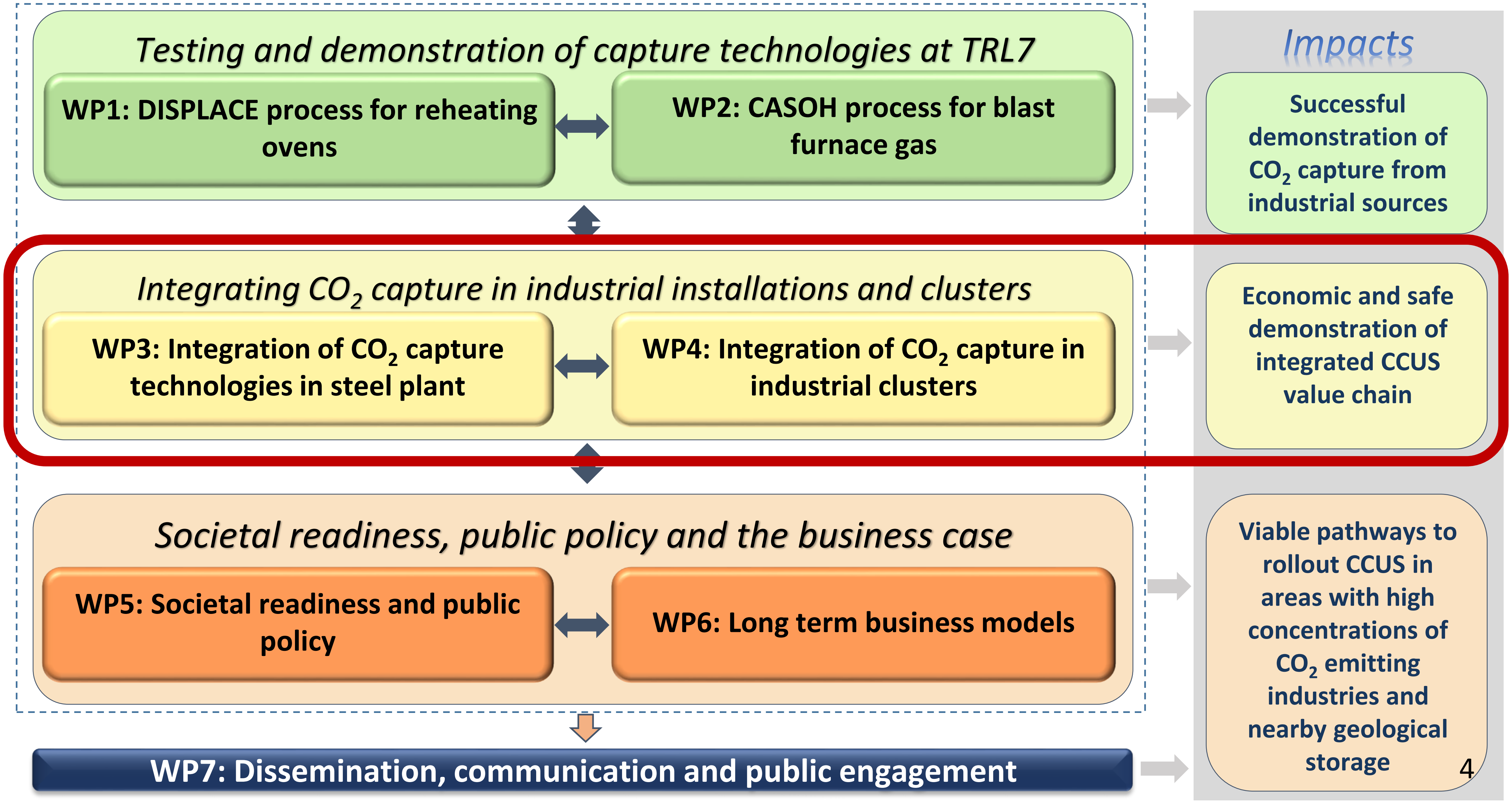
- Elevate two promising CO_2 solid based capture technologies from TRL5 to TRL7 & design for optimal integration in the steel industry
- Analyse the economic, environmental and business impacts of large scale process as part of the North Sea Port industrial cluster including CO_2 quality for the pipeline transportation & storage infrastructure
- Develop and test approaches with stakeholders and end-users to assess and advance societal readiness for CCUS in industrial clusters



Map courtesy of Thomas Desnijder, North Sea Port, Gent, Belgium.

C⁴U

C^4U PERT Diagram



Presentation overview

- C^4U processes integrated in the steel mill
- The selection of the benchmark processes and their techno-economic performance
- The integration of the C^4U in industrial clusters: challenge and opportunity
- Conclusions

WP 3 - Integration of CO_2 capture technologies in steel plant

POLITECNICO MILANO 1863

ArcelorMittal

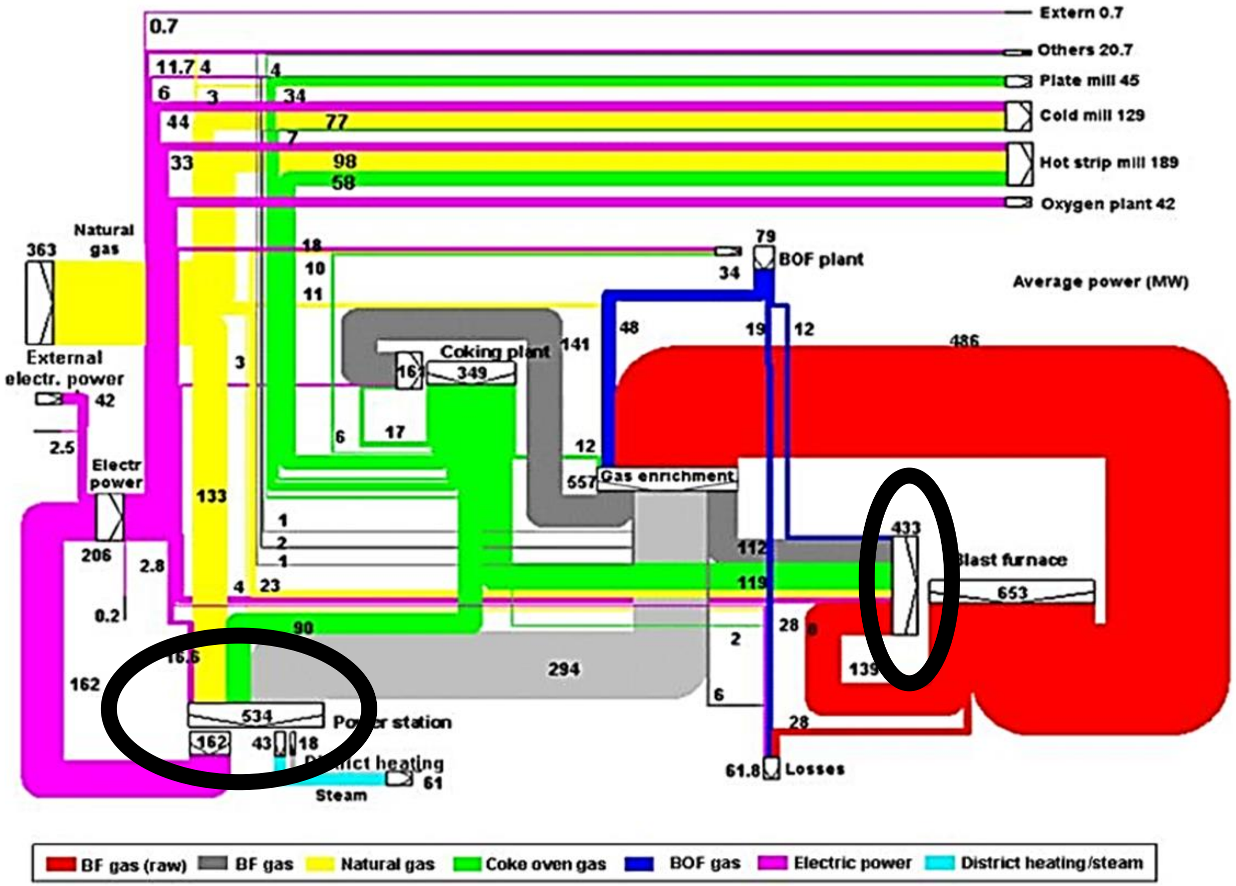
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

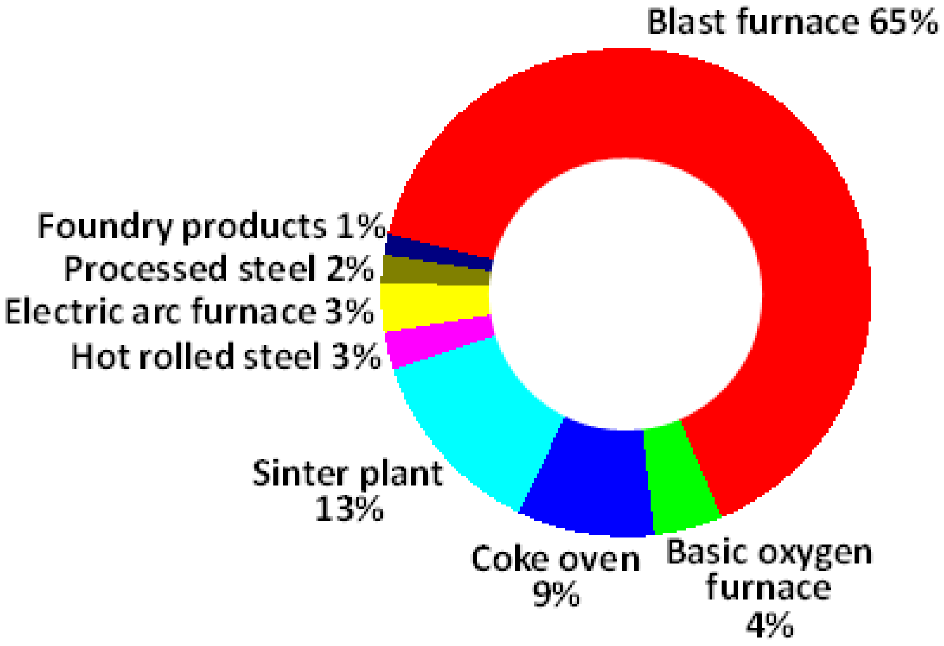
MANCHESTER 1824
The University of Manchester

TNO innovation for life

wood.

Integrated steelworks: a complex plant



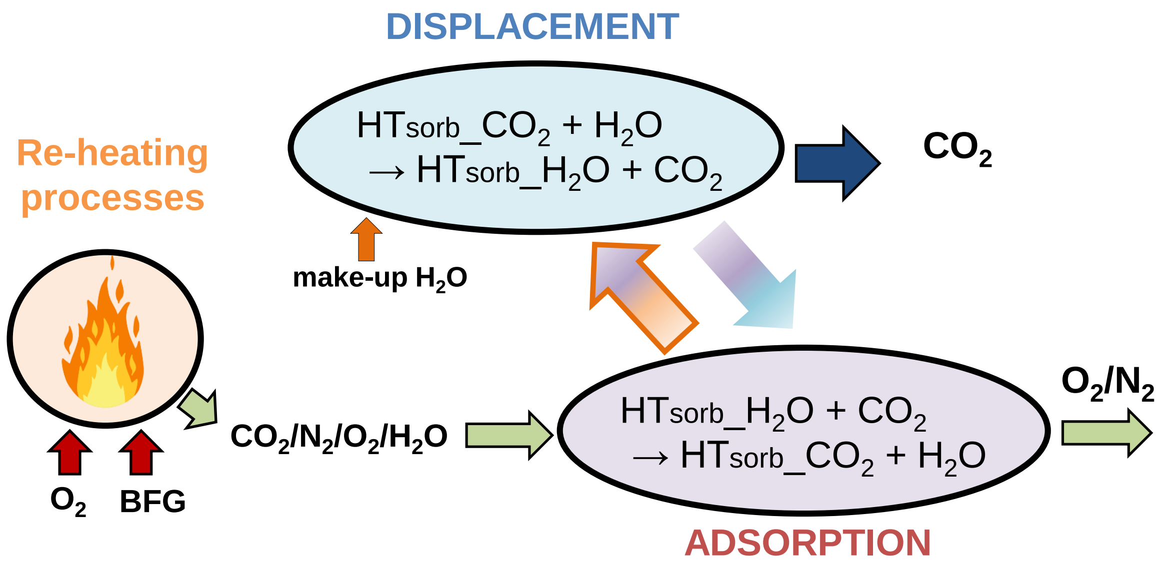


Breakdown of contribution to CO_2 emissions

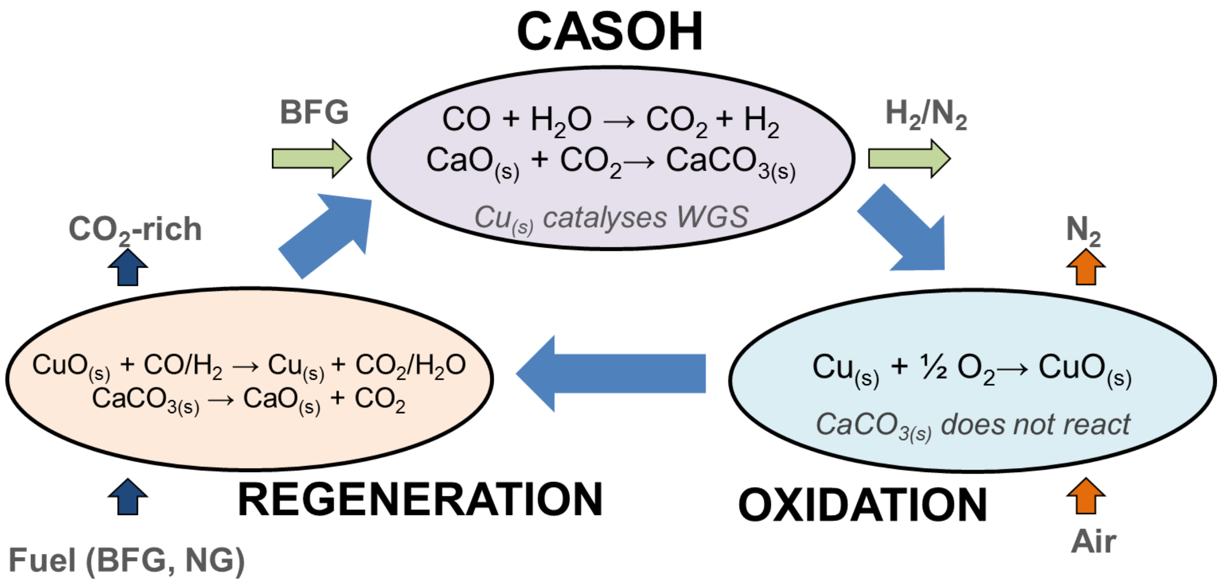
R. Remus, S. Roudier, M. a. Aguado Monsonet, and L. D. Sancho, *Best Available Techniques (BAT) Reference Document for Iron and Steel Production*, vol. BREF-IS. 2013. Methodology for the free allocation of emission allowances in the EU ETS Post 2012–Sector report for the iron and steel industry. Ecofys, Fraunhofer ISI and Öko-Institute, November 2009.

C⁴U gas-solid technologies

DISPLACE



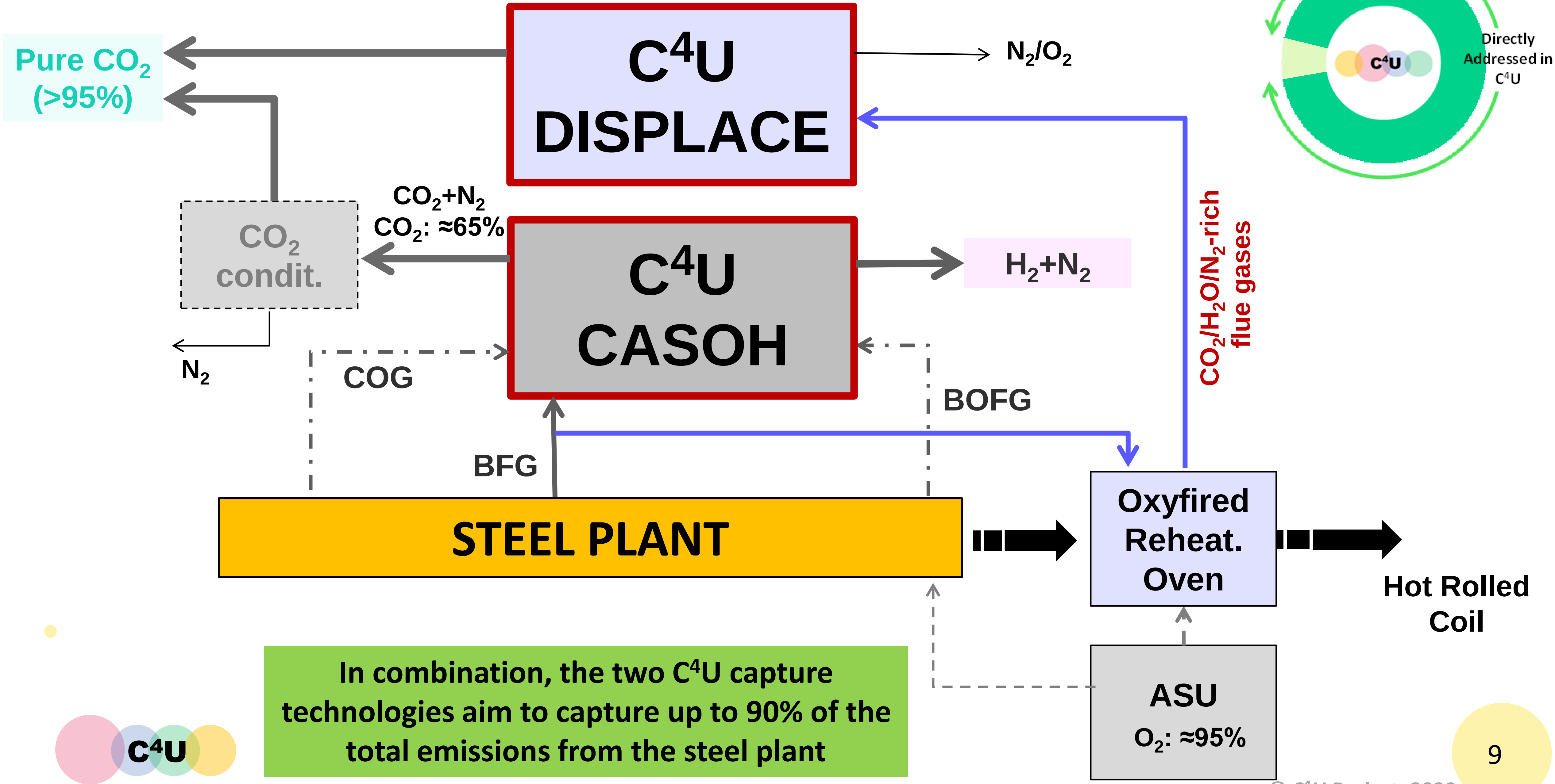
CASOH



More details will be available tomorrow: ***SESSION 3B*** *12.45-13.05* (CET)

P. Cobden, C. Abanades - Pilot preparation for demonstration in the C⁴U project

WP3: C4U CONCEPT AND INTEGRATION



WP3: METHODOLOGY

Task 3.1
- Methodology for the techno-economic assessment
- Reference case definition
- CO_2 capture process modelling (process design)

Task 3.2
- Parametric performance of the CO_2 capture technologies, both the reference and the C^4U ones
- SPECCA and Cost of CO_2 avoided

Task 3.3
- Process design package for a full scale
- Cost estimation of the capture processes

Task 3.4
- The optimal integration of the C^4U technologies in the integrated steel plant
- Determine the energy (SPECCA) and costs (Cost of CO_2 avoided) for the C^4U technologies at defined CO_2 avoidance rates and CO_2 purities.

C^4U

WP3: METHODOLOGY

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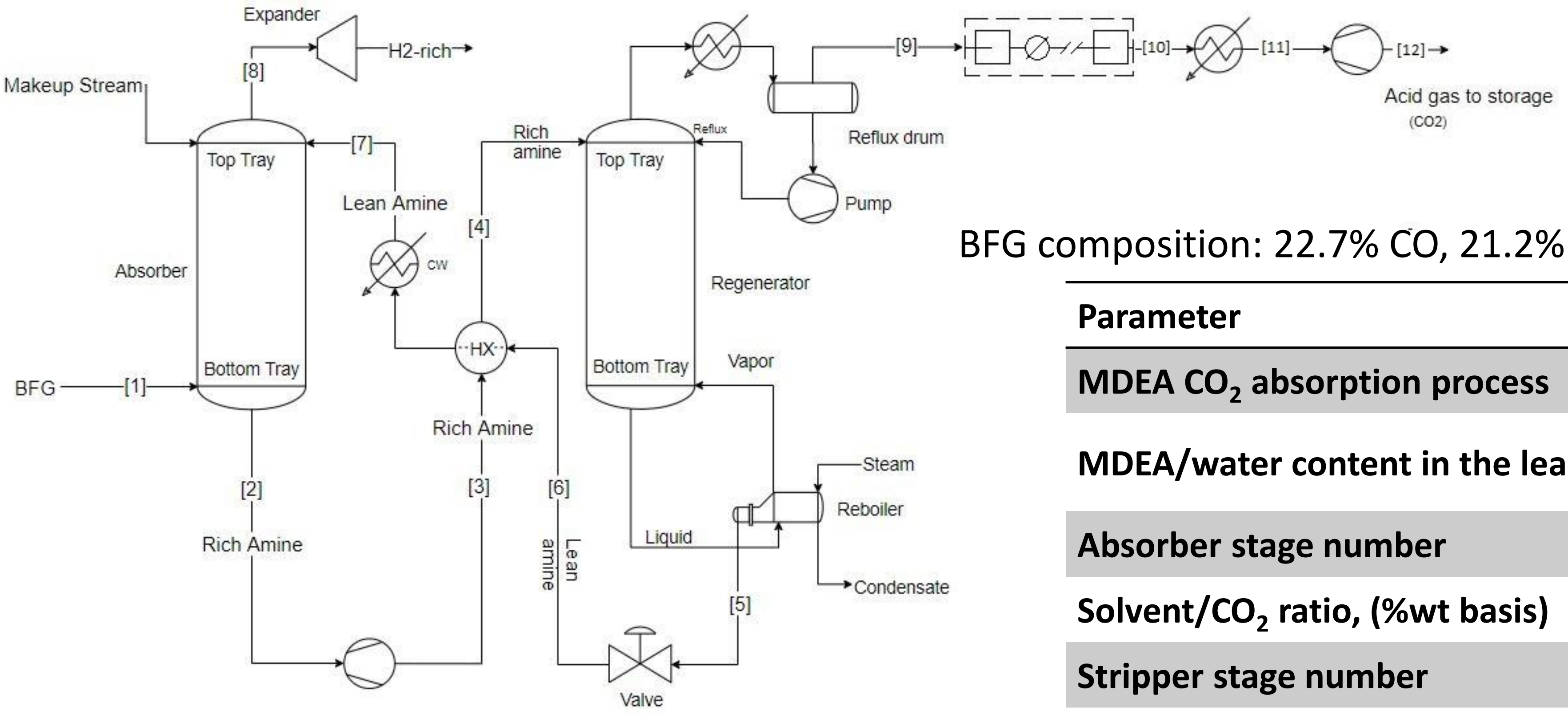
Benchmark process: MDEA pre-combustion separation – Base case



Plant size: 3.16 $Mton_{HRC}/y$

BFG flow rate: 125.1 kg/s

BFG composition: 22.7% CO, 21.2% CO_2, 2.4% H_2, 53.5% N_2, 0.2% C_2H_4

Parameter	Value
MDEA CO_2 absorption process	
MDEA/water content in the lean solvent (%wt)	25/72
Absorber stage number	20
Solvent/CO_2 ratio, (%wt basis)	3/25
Stripper stage number	20
Steam condition at the reboiler (bar)	6.0
CO_2 delivery pressure (bar)	110
CO_2 delivery temperature (°C)	25

DCF : 27.4% CO, 0.9% CO_2, 2.9% H_2, 64.7% N_2, 0.2% C_2H_4, 3.7% H_2O

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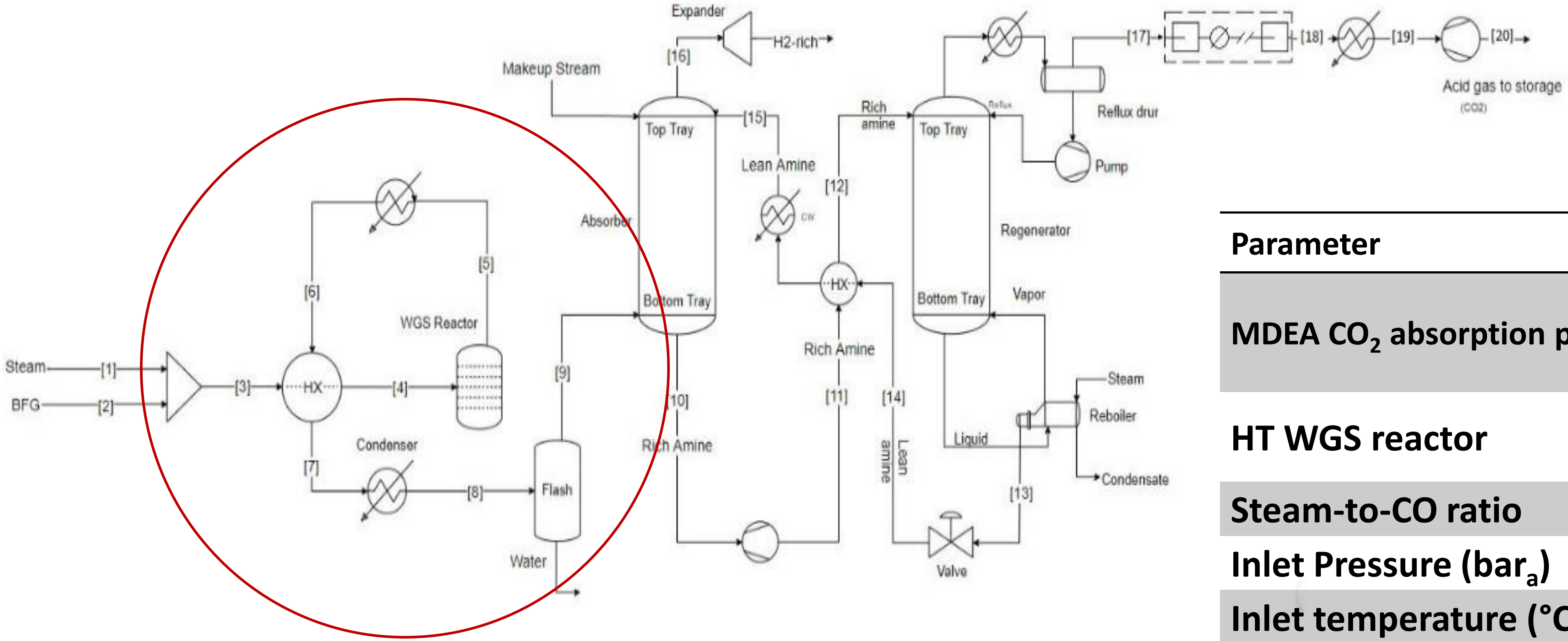
Benchmark process: MDEA pre-combustion separation – Enhanced Capture



Parameter	Value
MDEA CO_2 absorption process	Same as before
HT WGS reactor	
Steam-to-CO ratio	1.5
Inlet Pressure (bar_a)	2.9
Inlet temperature (°C)	300
CO conversion (calculated at the equilibrium)	76.3%

DCF : 6.3% CO, 2.2% CO_2, 23.9% H_2, 61.8% N_2, 5.5% H_2O

METHODOLOGY: MAIN INDEXES

CO_2 capture rate of the technology

$$CCR[\%] = 1 - \frac{\left(\dot{N}_{CO_2} + \dot{N}_{CO} + \sum \zeta_c \cdot \dot{N}_c\right)_{out}}{\left(\dot{N}_{CO_2} + \dot{N}_{CO} + \sum \zeta_c \cdot \dot{N}_c\right)_{in}}$$

Levelized Cost of Decarbonized Fuel

$$LCODF\left[\frac{€}{GJ}\right] = \frac{TAC\left[\frac{M€}{y}\right]}{\dot{m}_{DCF} \times LHV_{DCF} \times h/y} \times 1000$$

Specific Primary Energy Consumption for CO_2 Avoided

$$SPECCA\left[\frac{MJ_{LHV}}{kg_{CO_2}}\right] = \frac{\left(\frac{1}{\eta_{capture}} - \frac{1}{\eta_{no,capt}}\right)}{E_{CO_2,no\ capt} - E_{CO_2,capture}}$$

CO_2 avoidance cost

$$CCA\left[\frac{€}{t_{CO_2}}\right] = \frac{LCODF_{Capture} - LCODF_{ref}}{E_{CO_2,ref} - E_{CO_2,capture}}$$

Additional cost of HRC for decarbonised steel mill

$$\Delta C_{HRC}\left[\frac{€}{t_{HRC}}\right] = \frac{TAC_{capture} + \Delta C_{el,capture} - TAC_{no\ capt}}{\dot{m}_{HRC}}$$

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PERFORMANCE COMPARISON – TECHNO-ECONOMICS

	Unit	no capture	Base case	Enhanced
Steel mill size	Mt_{HRC}/y	3.16	3.16	3.16
Carbon Capture Rate	[%]		46%	83%
Cold gas efficiency	[%]	100.0%	100.0%	90.5%
Overall energy efficiency	[%]	100.0%	81.8%	56.7%
CO_2 specific emissions	$[kg_{CO2}/GJ_{LHV}]$	267.1	153.38	51.19
CO_2 capture avoidance	[%]		42.6%	80.8%
ΔCO_2 specific emissions[a)]	$[kg_{CO2}/t_{HRC}]$	711.9	383.56	120.28
SPECCA	$[MJ_{LHV}/kg_{CO2}]$		1.96	3.54

	Unit	no capture	Base case	Enhanced
LCODF	[€/GJ]	5.20	9.73	14.78
Δcost of HRC	$[€/t_{HRC}]$		11.99	21.65
CO_2 avoidance cost	$[€/t_{CO2}]$		39.84	49.38

WP4 - Integration of CO_2 Capture in Industrial Clusters

WP4: OBJECTIVES

Cluster 3 industrial port areas North Sea Port, Port of Antwerp and Port of Rotterdam responsible of 1/3 or CO_2 emissions from Benelux, approx. 60 Mt/a

Define common CO_2 transportation infrastructure for geological storage up to 10 Mt CO_2/a in the depleted gas fields (P18 fields)

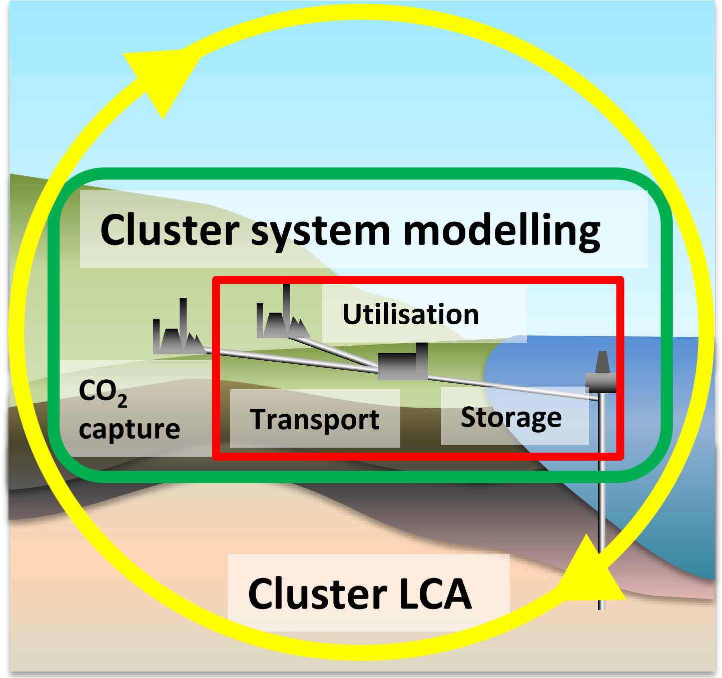
Perform the whole economic, safe and environmental LCA of the integrated industrial cluster of the North Sea Port area.

WP4 - INTEGRATION OF CO_2 CAPTURE IN INDUSTRIAL CLUSTERS

Task 4.1 Transport, utilisation and storage safety and operability impacts Experimental and computational studies to evaluate the impacts of impurities in the CO_2 streams captured from steel plants, on the CO_2 utilisation, transport and storage

Task 4.2 CCUS cluster whole-system modelling and operational logistics techno-economic evaluation to assess energy and cost penalties as a function of the CO_2 purity in the North Sea Port cluster for 2030 and 2050 decarbonisation scenarios.

Task 4.3 Life Cycle Assessment (LCA) of the North Sea Port CCS cluster LCA assessment of the environmental impact of the North Sea Port CCS cluster.



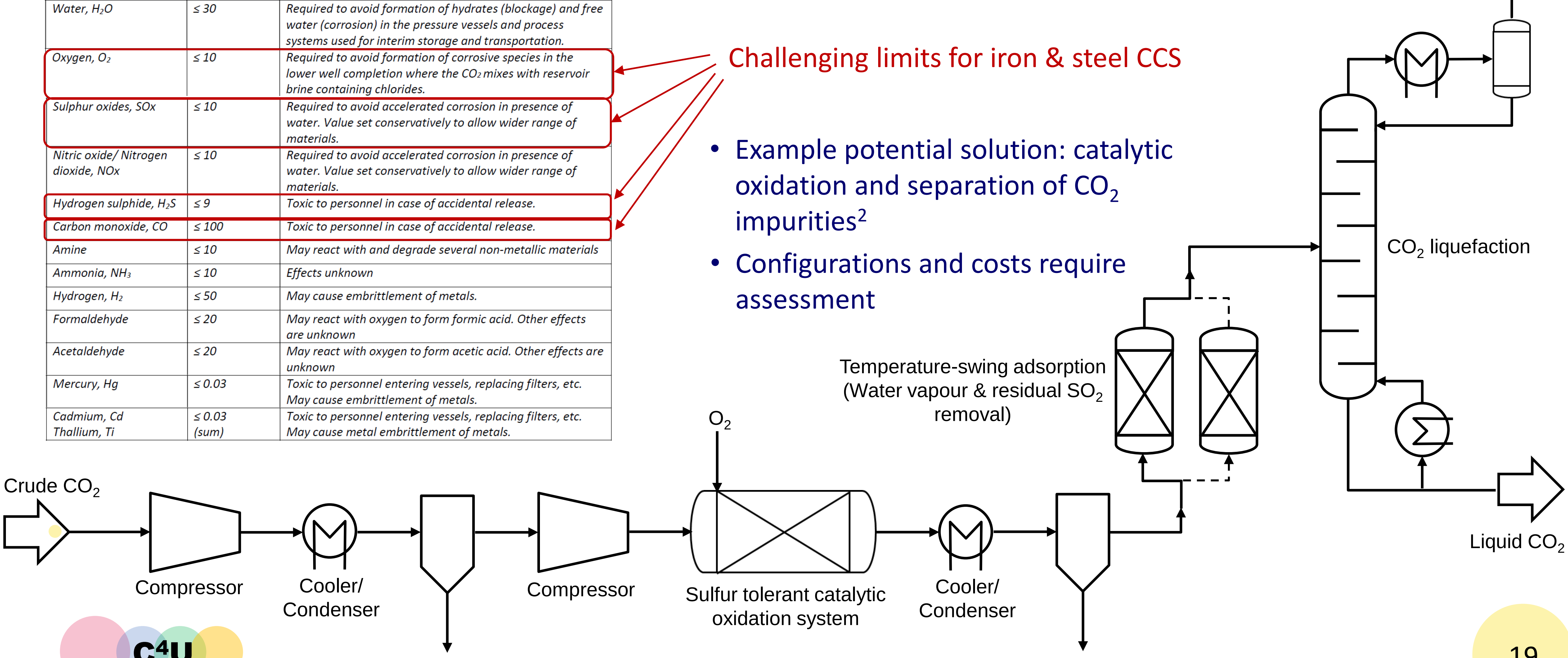
WP4: CO_2 purification challenge

European CO_2 quality specifications; e.g. Northern Lights[1]

Component	Concentration ppm (mole)	
Water, H_2O	*≤ 30*	*Required to avoid formation of hydrates (blockage) and free water (corrosion) in the pressure vessels and process systems used for interim storage and transportation.*
Oxygen, O_2	*≤ 10*	*Required to avoid formation of corrosive species in the lower well completion where the CO_2 mixes with reservoir brine containing chlorides.*
Sulphur oxides, SOx	*≤ 10*	*Required to avoid accelerated corrosion in presence of water. Value set conservatively to allow wider range of materials.*
Nitric oxide/ Nitrogen dioxide, NOx	*≤ 10*	*Required to avoid accelerated corrosion in presence of water. Value set conservatively to allow wider range of materials.*
Hydrogen sulphide, H_2S	*≤ 9*	*Toxic to personnel in case of accidental release.*
Carbon monoxide, CO	*≤ 100*	*Toxic to personnel in case of accidental release.*
Amine	*≤ 10*	*May react with and degrade several non-metallic materials*
Ammonia, NH_3	*≤ 10*	*Effects unknown*
Hydrogen, H_2	*≤ 50*	*May cause embrittlement of metals.*
Formaldehyde	*≤ 20*	*May react with oxygen to form formic acid. Other effects are unknown*
Acetaldehyde	*≤ 20*	*May react with oxygen to form acetic acid. Other effects are unknown*
Mercury, Hg	*≤ 0.03*	*Toxic to personnel entering vessels, replacing filters, etc. May cause embrittlement of metals.*
Cadmium, Cd Thallium, Ti	*≤ 0.03 (sum)*	*Toxic to personnel entering vessels, replacing filters, etc. May cause metal embrittlement of metals.*

Challenging limits for iron & steel CCS

- Example potential solution: catalytic oxidation and separation of CO_2 impurities[2]
- Configurations and costs require assessment

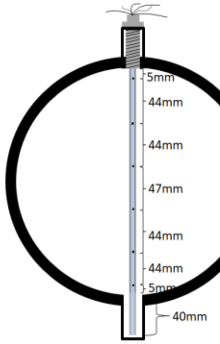


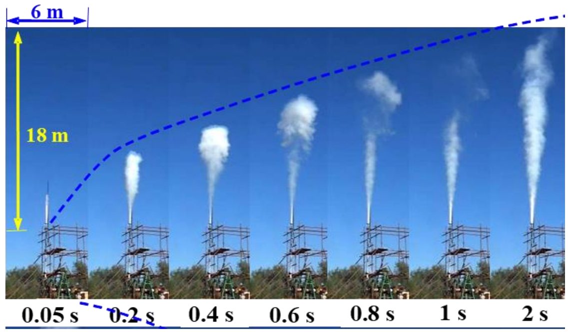
[1] Norwegian CCS Demonstration Project Norcem FEED, https://ccsnorway.com/ [2] Praxair. EP0952111A1. CO_2 purification system, 1999.

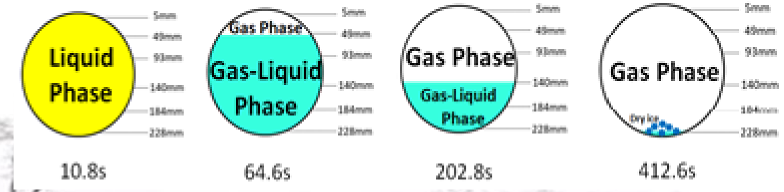
PIPELINE DECOMPRESSION EXPERIMENTS

OBJECTIVES

This task involves performing controlled pipeline decompression tests to assess the risk of solid CO_2 formation and transition to two-phase flow







Medium-scale test pipeline 40 m long, 2'' i.d. (INERIS)

Large-scale test pipeline 256 m long, 233 mm i.d. (DUT)

CONCLUSIONS

The C^4U project will assess two advanced CO_2 capture technologies with respect to the solvent-based process which currently costs 50 €/tonCO_2 with a maximum capture efficiency of 83%

The sensitivity analysis at large scale on C^4U technologies will include feedstock quality and CO_2 quality uses interlinking 2 WPs

The study will focus specifically on 3 industrial port areas North Sea Port, Antwerp and Rotterdam responsible of 1/3 or CO_2 emissions from Benelux, approx. 60 Mt/a

Perform the whole economic, safe and environmental LCA of the integrated industrial cluster of the North Sea Port area

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Advanced Carbon Capture for Steel Industries Integrated in CCUS Clusters

THANK YOU

Questions ?

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884418

Advanced Carbon Capture for Steel Industries Integrated in CCUS Clusters

Supplementary slides

The contents of this presentation are the responsibility of University of Manchester & University College London and do not necessarily reflect the opinion of the European Union.

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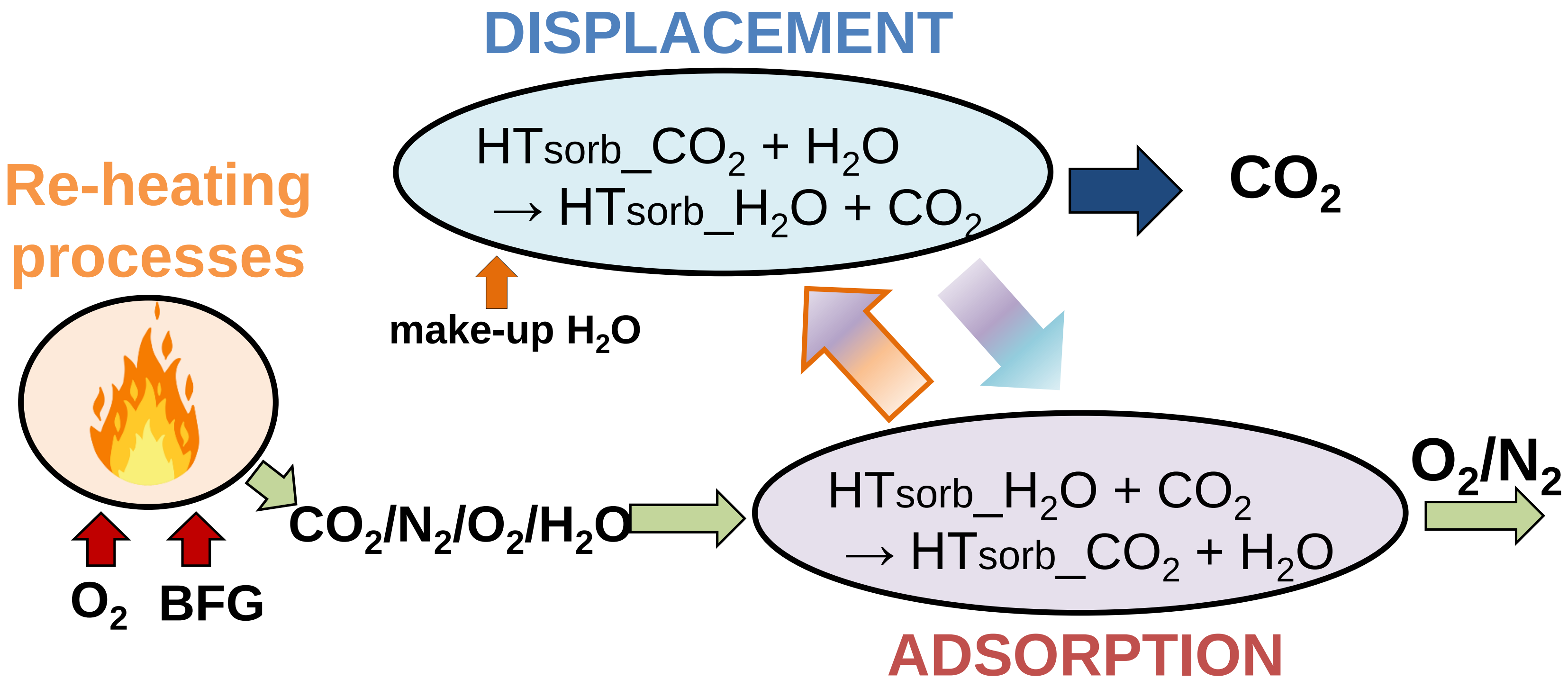
DISPLACE: High temperature sorption-displacement process using hydrotalcites for CO_2 sorption and recovery of steam



**shown above for CO_2 recovery from oxy-combustion use of Blast Furnace Gas*

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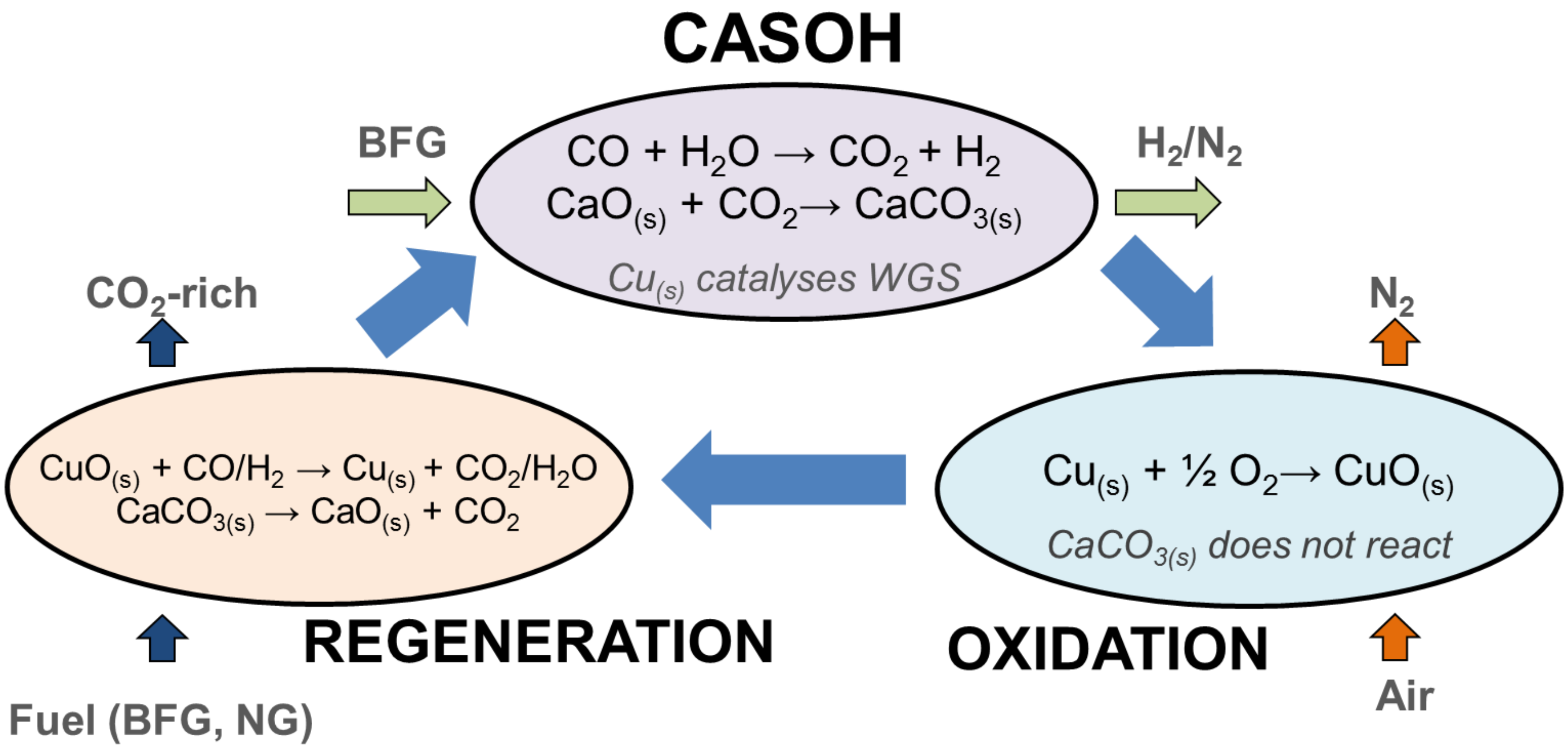
CASOH: Calcium Assisted Steel mill Off-gas Hydrogen process for blast furnace gas



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PERFORMANCE COMPARISON - TECHNICAL

	Base case	Enhanced
Total Fuel Input (MW)	294.67	294.67
Net power consumption (MW)	14.9	33.7
CO_2 flow rate for storage (kg/s)	36.5	65.8
Specific electricity demand (kWh/kg_{CO2})	0.113	0.142
Reboiler heat duty (MW)	50.1	91.4
Reboiler heat duty/CO_2 flow rate for storage (MJ/kg_{CO2})	1.3	1.3
Required heat for WGS (MW)	-	66.5
CO_2 capture efficiency (%)	46.5	83.80
CO_2 purity for storage (%)	98.2	98.1
Thermal energy output (DCF)(MW)	294.61	266.80

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PERFORMANCE COMPARISON – TECHNICAL

	Unit	no capture	Base case	Enhanced
Steel mill size	Mt_{HRC}/y	3.16	3.16	3.16
Thermal input (BFG LHV)	[MW]	294.67	294.67	294.67
Thermal output (decarbonised fuel LHV)	[MW]	294.67	294.61	266.80
Heat requirements	[MW]		50.62	142.47
Electricity requirements	[MW]		14.90	33.62
Carbon Capture Rate	[%]		46%	83%
Cold gas efficiency	[%]	100.0%	100.0%	90.5%
Overall energy efficiency	[%]	100.0%	81.8%	56.7%
CO_2 specific emissions	$[kg_{CO2}/GJ_{LHV}]$	267.1	153.38	51.19
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PERFORMANCE COMPARISON - ECONOMICS

	Unit	no capture	Base case	Enhanced
Steel mill size	Mt_{HRC}/y	3.16	3.16	3.16
MDEA unit	[M€]		37.10	56.65
WGS reactors+ heat exchangers	[M€]		0	12.36
Gas expander	[M€]		3.73	2.80
CO_2 compressor units	[M€]		16.66	19.98
Pumps	[M€]		0.02	0.02
Total Equipment Cost	[M€]		57.50	91.81
Total Direct Plant Cost	[M€]		117.31	187.29
Total Plant Cost	[M€]		155.14	247.69
Annualised Plant Cost	[M€/y]		17.69	28.24
Fuel Cost	[M€/y]	43.49	43.49	43.49
variable, heat and electricity	[M€/y]		12.44	27.78
fixed O&M	[M€/y]		7.76	12.38
Total Annualised cost	[M€/y]	43.49	81.37	111.9
LCODF	[€/GJ]	5.20	9.73	14.78
Δcost of HRC	[€/t_{HRC}]		11.99	21.65
CO_2 avoidance cost	[€/t_{CO2}]		39.84	49.38

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CONVERGE: CarbON Valorisation in Energy-efficient Green fuels

Green methanol synthesis for biodiesel production

16-17 th February, Converge Workshop

Objectives: Membrane assisted methanol synthesis

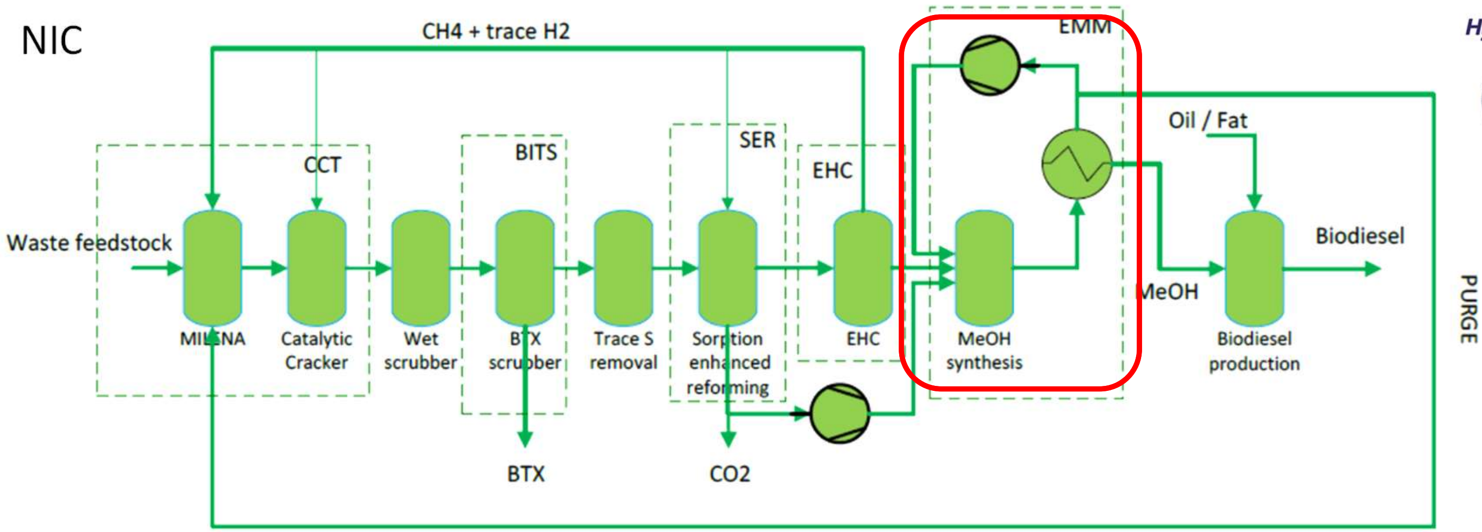
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 818135

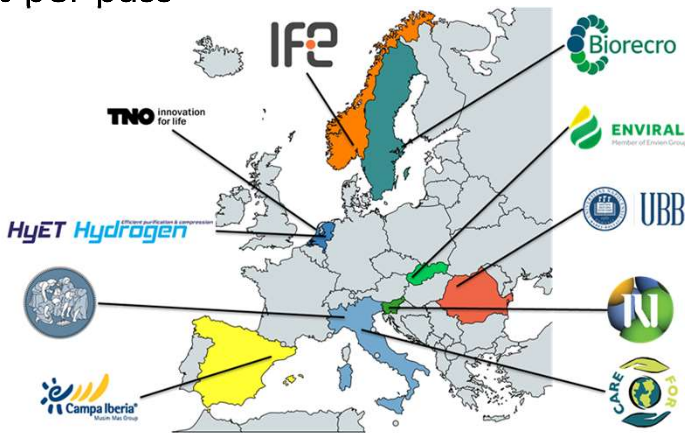
Membrane assisted methanol synthesis.

- Develop stable membranes at reaction conditions
- Develop multi-tube membrane reactor, targeted conversion for feed CO_2/H_2 33% per pass
- Demonstration of integrated process at TRL 5

Partners involved:

- TNO
- NIC



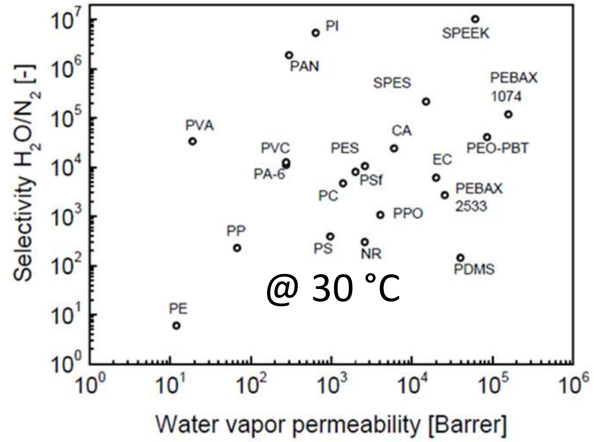


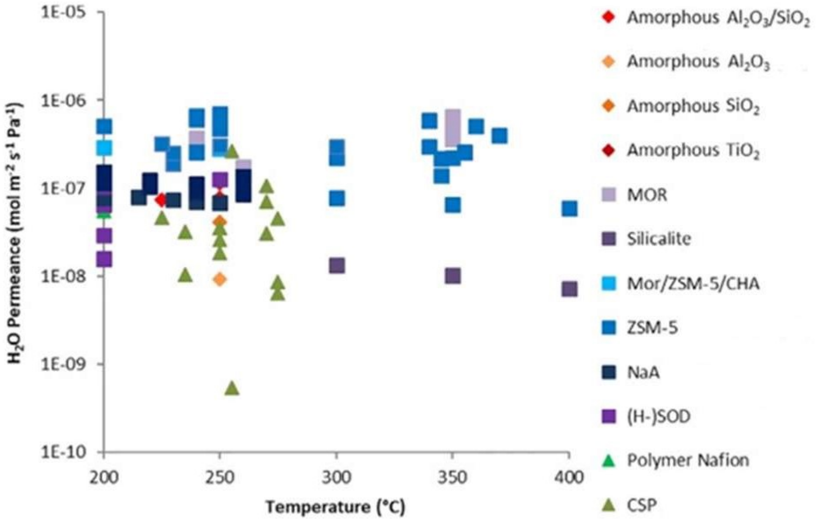
Membrane development - target

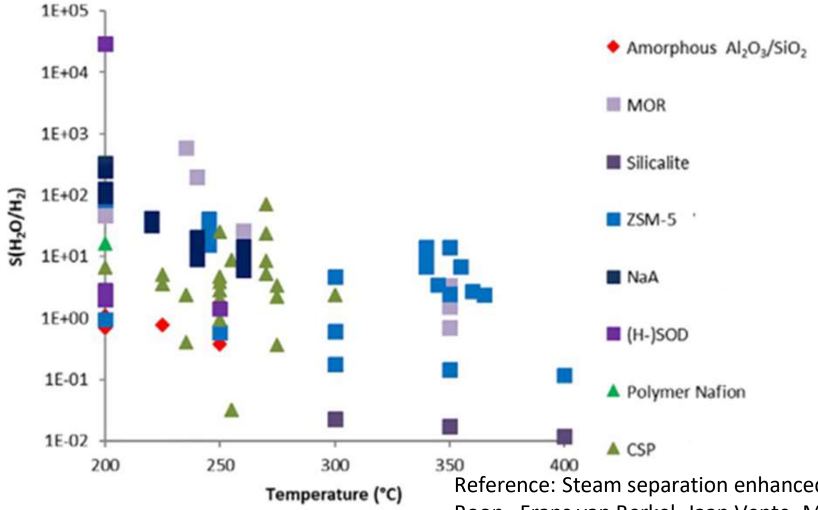
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 818135

Membrane development targets:

1) Stability at the methanol operating T and p (175-275°C), up to 100bar
2) High selectivity for steam and methanol
3) High steam/methanol permeability ➔ high flux







Reference: Steam separation enhanced reactions: Review and outlook, Jasper van Kampen, Jurriaa Boon , Frans van Berkel, Jaap Vente, Martin van Sint Annaland, Chemical Engineering Journal 374, 21019, 1286-1303

CONVERGE
CarbON Valorisation in Energy-efficient Green fuels

Inventory of suitable membranes

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 818135

• Amorphous microporous	APTES-PA (Aminopropyl triethoxysilane-Polyamide)
	BETSE (1, 2-bis (triethoxysilyl) ethane)
• Polymeric	SPEEK (sulfonated poly(ether ether ketone))
	PI (Poly Imides)
	PBI (Polybenzimidazol)
	PDMS (Polydimethylsiloxane)
	Li-Nafion

Membrane synthesis procedure -support

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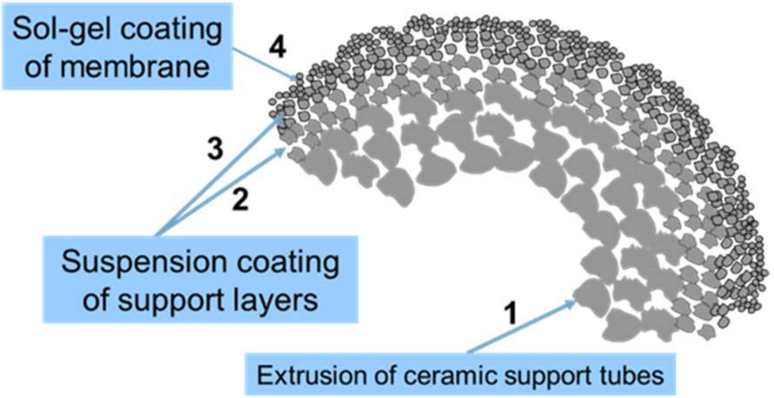
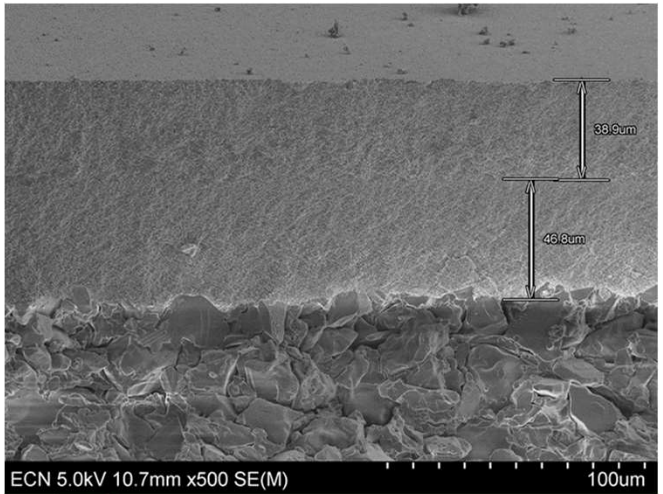
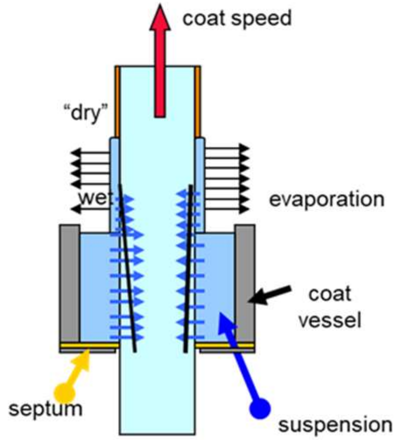
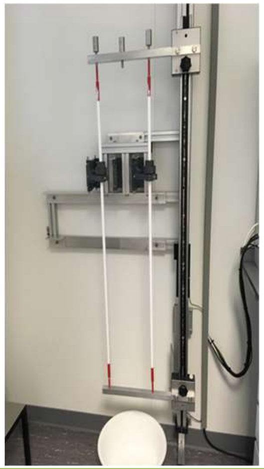


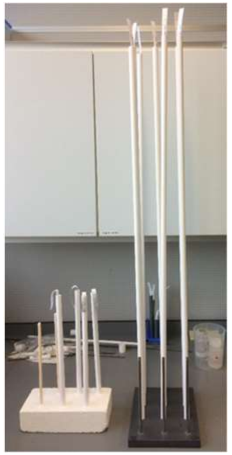
Membrane support layers

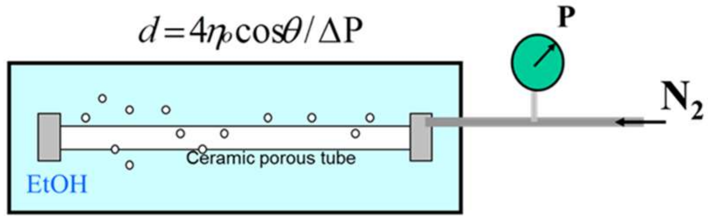




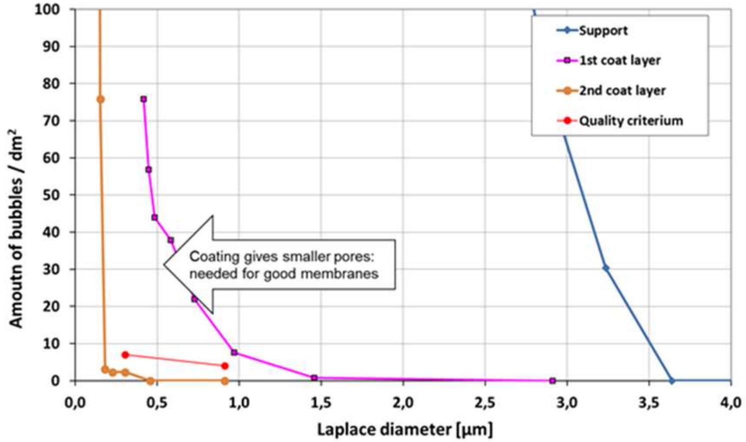
Coating process







Bubble point test



Results membrane separation tests

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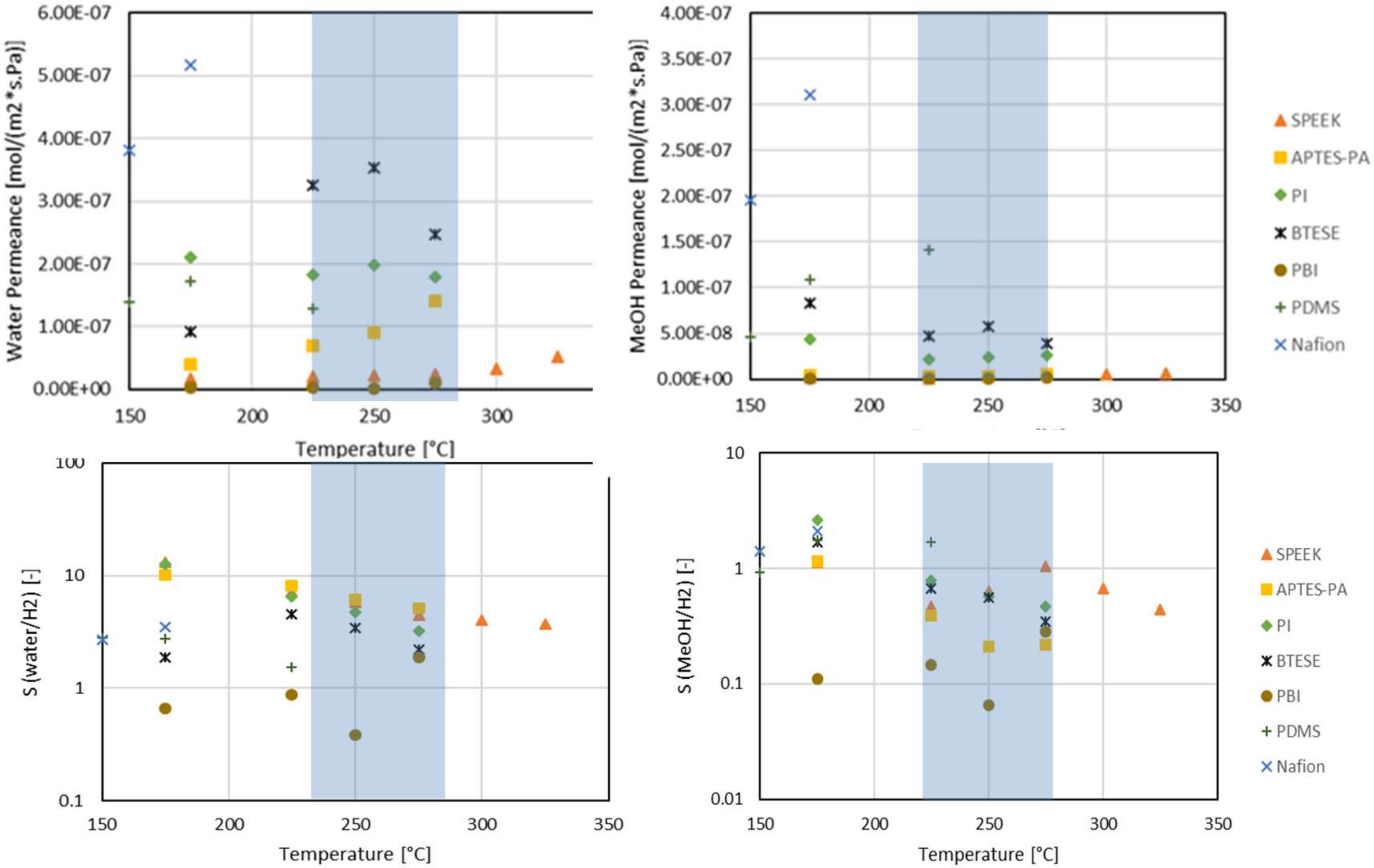


Test conditions:

- p_{feed} =35 bar, p_{perm} =1.5 bar, no sweep
- 60% H_2, 10% (50/50)methanol/steam, 20% CO_2, 1% CO, 9% N_2

Nafion, BETSE, PI highest steam and MeOH permeance

- BETSE performance decreases at 275°C, Nafion not selective at T>225°
- H_2O/H_2 selectivity highest for APTES-PA, SPEEK and PI
- $MeOH/H_2$ selectivity highest for PDMS 1.7, PI and BETSE ~ 0.6-0.8

Pre-selection:
1) PI
2) BETSE
3) APTES-PA

PDMS, Nafion ➔ no selectivity > 225 °C
SPEEK➔ low H_2O and MeOH permeance
(10X lower than PI)
PBI ➔ low permeance, low selectivity

CarbON Valorisation in Energy-efficient Green fuels

Conclusions

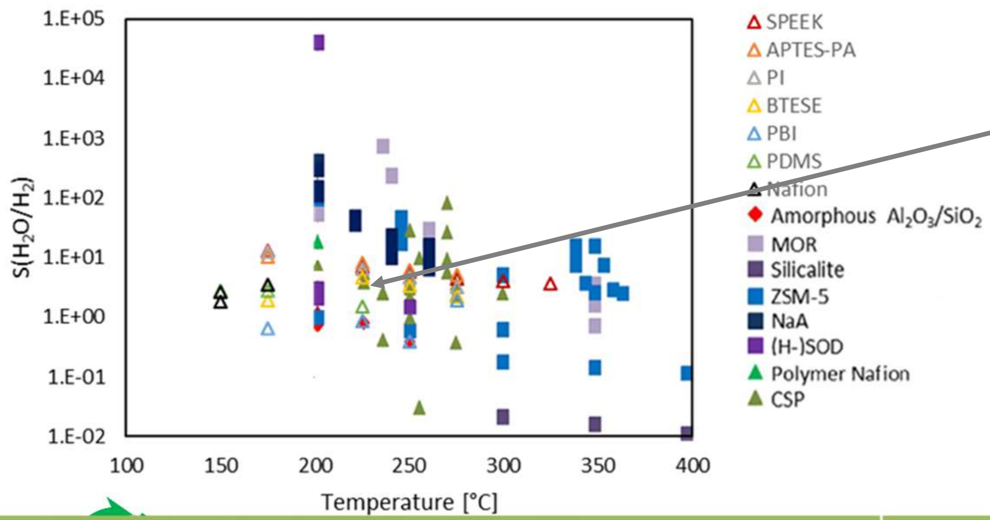
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 818135

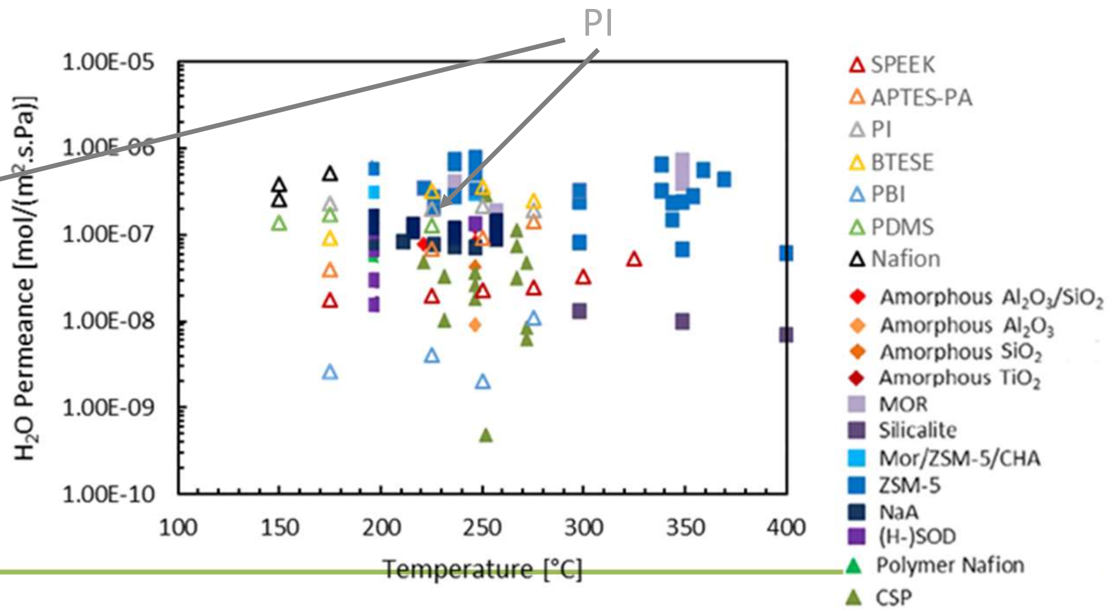
- PI membrane preselected as the most promising to reach conversion targets. Membrane performance comparison steam/MEOH/mix (T_{range} =225-250 °C)

	PI	BETSE	APTES
• H_2O/H_2 selectivity:	4.7-6.5	3.5-4.3	6-8
• $MEOH/H_2$ selectivity:	0.6-0.8	0.6-0.7	0.2-0.4
• H_2O permeance:	PI	1.6·PI	PI/2.3
• MeOH permeance:	PI	2.2·PI	PI/8.4

$H_2O > H_2 > MEOH > CO_2 > CO \approx N_2$

- Steam/H_2 behaviour compares well to literature



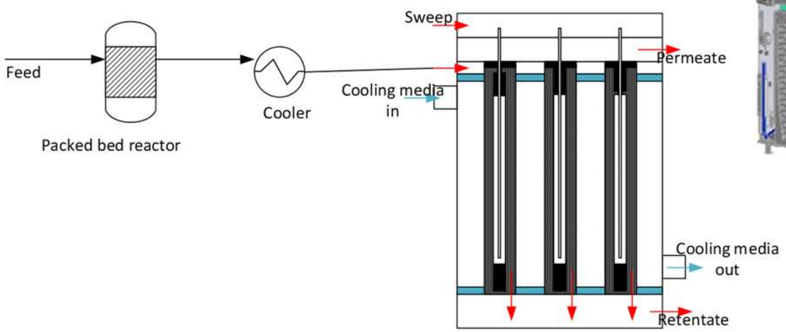


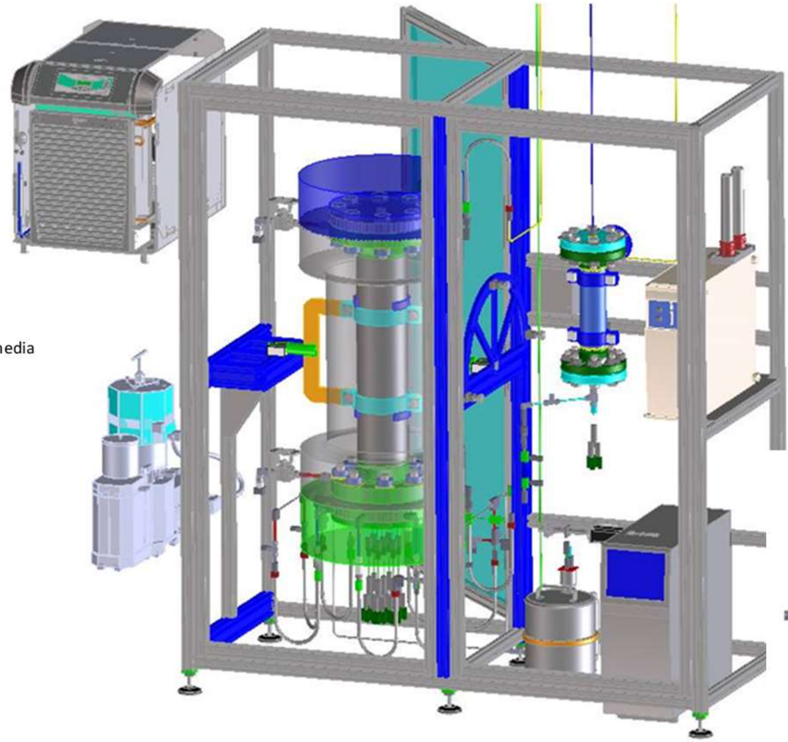
Next steps

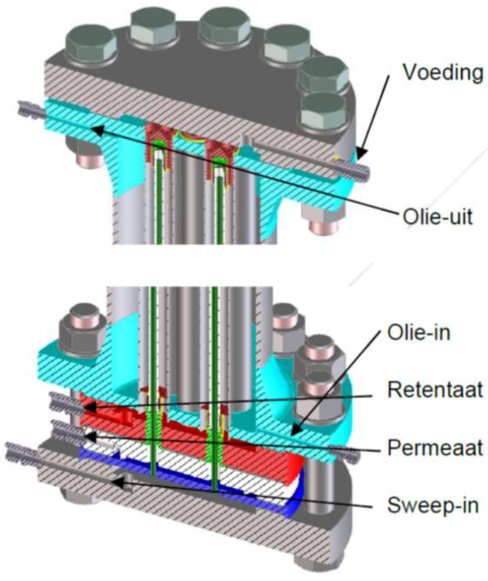
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 818135

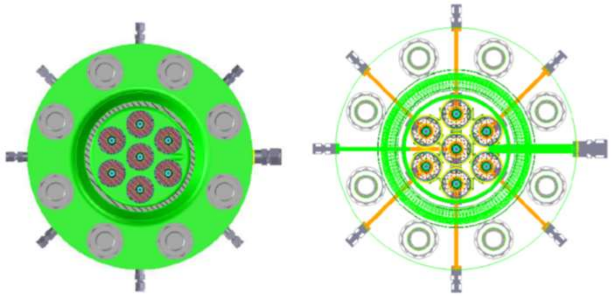
- Testing of preselected membranes in one tube membrane reactor
- Construction and testing of multi-tubular membrane reactor

Feed flow = 45 Nm^3/min





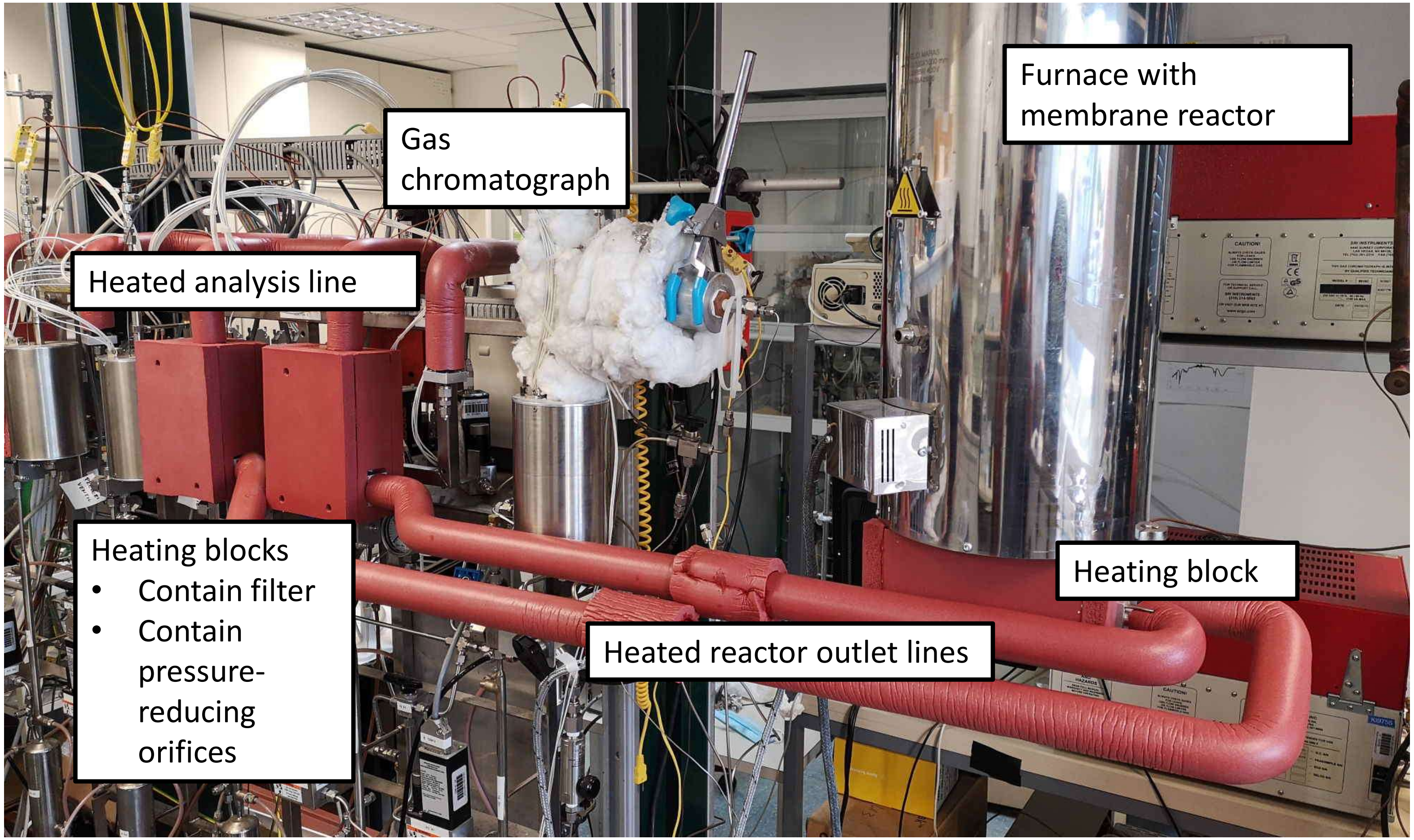




This project has received funding from the European Union's Horizon 2020
research and innovation programme under grant agreement No. 818135

Testing rig upgrade at NIC

- Testing of the prominent membranes supplied by TNO.
- Advantages of NIC system:
    - high pressure op. (80 bar) and
    - high temperature op. (350°C).



CONVERGE
CarbON Valorisation in Energy-efficient Green fuels

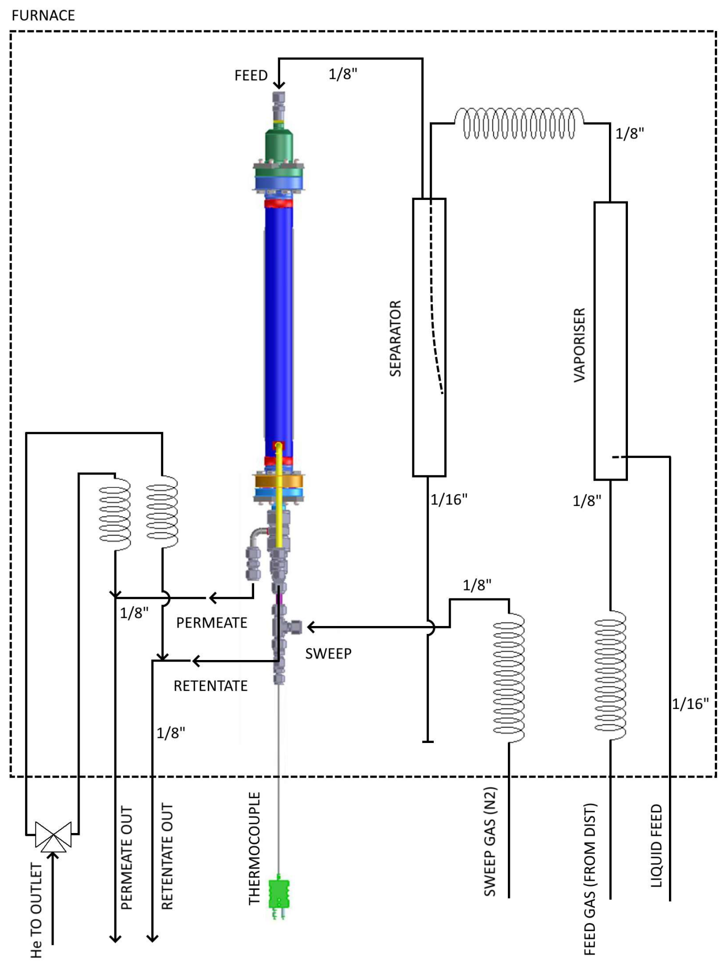
This project has received funding from the European Union's Horizon 2020
research and innovation programme under grant agreement No. 818135

Inside the furnace with the membrane module

- Feed gas saturation with H_2O or MeOH to:
  - determine permeation and
  - simulate thermodynamical equibrium gas mixture.

- He dillution to determine in-situ flow rates of permeate and retentate by gas chromatography.

- CO_2 is pumped into the feed gas using HPLC pump before membrane module.



This project has received funding from the European Union's Horizon 2020
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Modelling procedure

Selected membrane characteristics
- Permeances for all compounds
- T and P dependence
- Determined empirically

Reaction kinetics for the selected catalyst
- Packed-bed reactor kinetic catalytic tests
- Regression of kinetic data using a PBR model (already developed)

Membrane reactor model

Mass transport phenomena
- Convection
- Diffusion
- Permeation through the membrane

Reaction phenomena
- Catalytic surface microkinetic reactions
- Adsorption/desorption

Model validation
- Catalytic experiments in membrane reactor

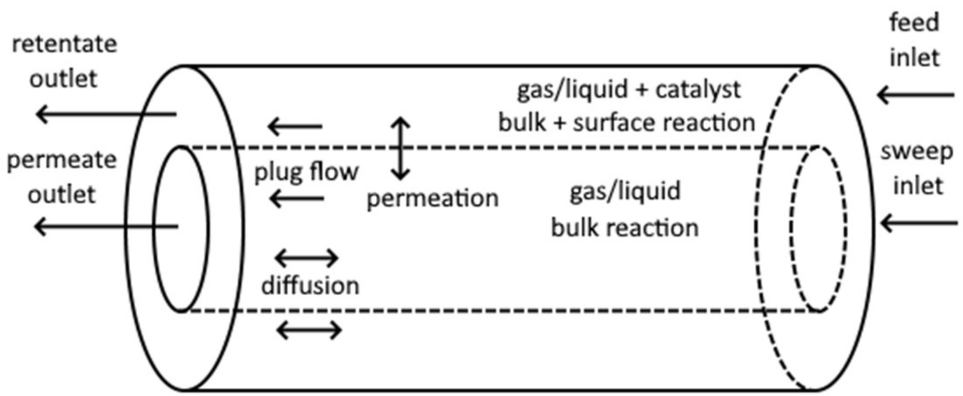
Exploration of different operating windows
- Inlet composition
- Temperatures
- Pressures
- Reactor geometry and size

Process optimization

Multi-tube system modelling

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 818135

Model development



Retentate MB: $$\frac{\partial C_i}{\partial t} = -v_{x,ret}\frac{\partial C_i}{\partial x} + \frac{D_i}{\tau}\frac{\partial^2 C_i}{\partial x^2} + C^*\frac{1-\varepsilon}{\varepsilon}R_{i,cat} + R_{i,bulk} - \frac{\dot{N}_{memb.}}{V_{ret}\,\varepsilon}$$

Permeate MB: $$\frac{\partial C_i}{\partial t} = -v_{x,perm}\frac{\partial C_i}{\partial x} + D_i\frac{\partial^2 C_i}{\partial x^2} + R_{i,bulk} + \frac{\dot{N}_{memb.}}{V_{perm}}$$

Flow through the membrane: $$\dot{N}_{memb.} = A_{memb.}P_i\left(p_{i,ret} - p_{i,perm}\right) = A_{memb.}P_iRT\left(c_{i,ret} - c_{i,perm}\right)$$

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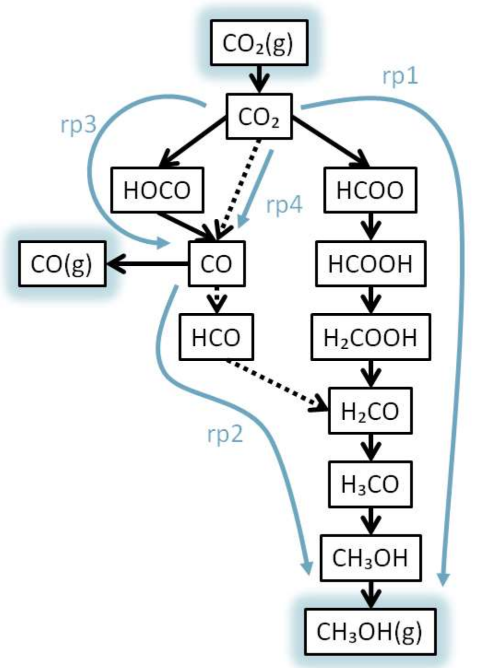
Model development: Kinetics of MeOH synthesis



Overall reaction scheme. Black arrows represent the elementary reaction steps and blue arrows the reaction pathways. Reaction species in black squares without "(g)" are adsorbed on the catalyst's surface.

- Surface reaction mechanism for methanol synthesis on CuZnAl
- Active sites: Cu (&), Zn (*)
- 5 gas phase species, 11 surface species
- 16 reversible surface reactions, 5 of which are adsorption/desorption reactions
- The constants obtained from literature were fitted to experimental data

	optimized				original Zn/Cu(211)			
Reaction	Afor [s-1]	Eafor [kJ/mol]	Aback [s-1]	Eaback [kJ/mol]	Afor [s-1]	Eafor [kJ/mol]	Aback [s-1]	Eaback [kJ/mol]
H2 + & + & ⇌ H& + H&	1.00E+03	51.00	1.77E+12	78.00	1.00E+03	51.00	1.77E+12	78.00
H& + CO2* ⇌ HOCO*&	4.62E+13	83.80	8.23E+13	104.28	3.91E+12	95.53	1.00E+11	123.51
H& + H2CO*& ⇌ H3CO*& + &	3.12E+08	8.47	1.17E+11	88.29	4.66E+12	11.58	1.00E+11	114.82
H& + H3CO*& ⇌ CH3OH*& + &	3.28E+12	112.01	6.98E+12	87.02	1.99E+14	143.77	1.44E+13	116.75
H& + CO2* ⇌ HCOO*&	1.69E+11	58.96	5.97E+14	142.86	3.57E+12	74.30	1.00E+11	188.16
H& + HCOO*& ⇌ HCOOH*& + &	4.69E+09	60.20	2.71E+10	75.73	7.93E+12	114.82	1.77E+11	48.25
H& + HCOOH*& ⇌ H2COOH*& + &	1.13E+12	87.74	6.71E+13	75.98	1.26E+12	58.86	9.57E+13	58.86
H2COOH*& + * ⇌ H2CO*& + OH*	1.82E+13	59.21	4.26E+11	17.08	2.53E+13	50.17	1.86E+11	16.40
H& + OH* ⇌ H2O*+ &	6.43E+09	72.66	2.89E+10	72.73	1.22E+13	77.19	4.83E+11	70.44
CO2* + & ⇌ CO& + O*	3.98E+12	46.16	1.57E+12	52.88	1.04E+13	76.23	8.40E+12	65.61
H& + O* ⇌ OH*+&	5.90E+12	309.13	5.05E+10	226.11	1.88E+13	116.75	1.00E+11	198.77
HOCO*& ⇌ CO& + OH*	3.16E+10	27.99	4.89E+11	65.23	6.60E+13	22.19	1.00E+11	58.86
CO2 + * ⇌ CO2*	7.53E+02	-2.29	2.9E+09	-29.13	7.41E+02	-2.01	1.00E+13	-30.88
CH3OH + * + & ⇌ CH3OH*&	2.59E+01	-0.99	1.34E+13	43.01	8.68E+02	-2.01	1.00E+13	39.56
H2O + * ⇌ H2O*	8.38E+02	-1.69	1.31E+12	39.45	1.16E+03	-2.01	1.00E+13	37.63
CO + & ⇌ CO&	2.86E+02	-0.98	3.25E+13	59.12	9.28E+02	-2.01	1.00E+13	98.42

Reactions and reaction rate constants (original from literature and fitted to experimental data)

CONVERGE
CarbON Valorisation in Energy-efficient Green fuels

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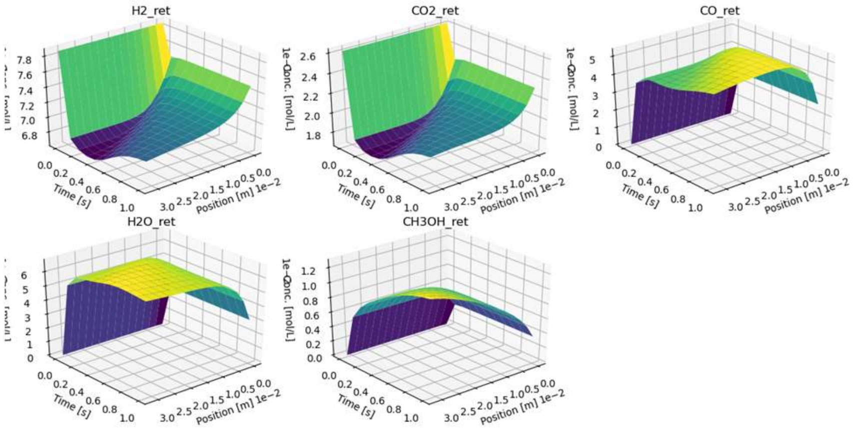
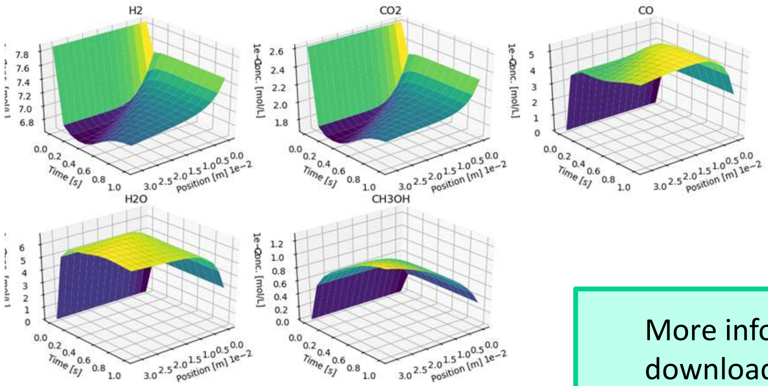
Model development

- Modeling in the programme CERRES developed at NIC

CERRES

- ✔ Simulation of 14 different types of chemical reactors (**including membrane reactor**)
- ✔ Complex user-defined chemical kinetics
- ✔ Model-experiment compare
- ✔ Parameter optimization
- ✔ Sensitivity analysis
- ✔ Efficient computation
- ✔ Plot results and export data
- ✔ Easy to use (graphical user interface)
- ✔ Free for academic/teaching use





More information and download available at:

www.cerres.org

CONVERGE
CarbON Valorisation in Energy-efficient Green fuels

Acknowledgements

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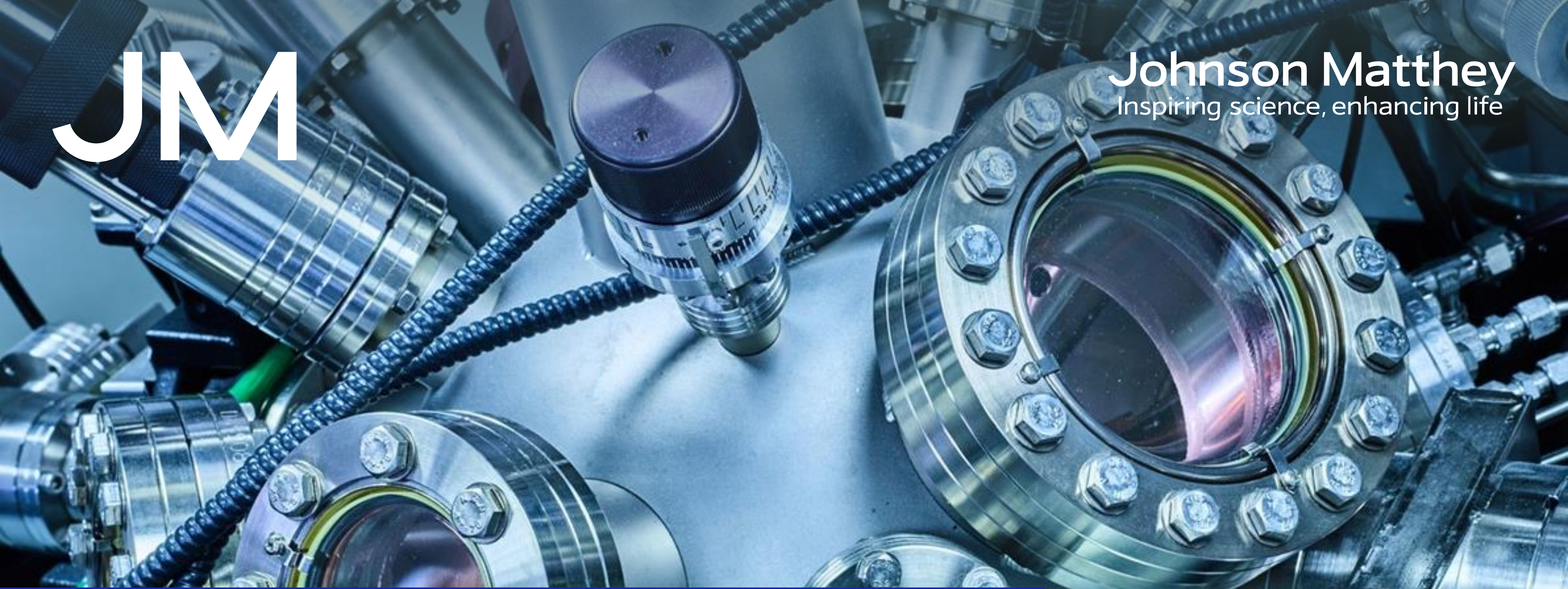
CONVERGE: CarbON Valorisation in Energy-efficient Green fuels

WP4: Green methanol synthesis for biodiesel production

Johnson Matthey
Inspiring science, enhancing life



Realising the potential of MOFs through efficient scale-up

Adam Deacon

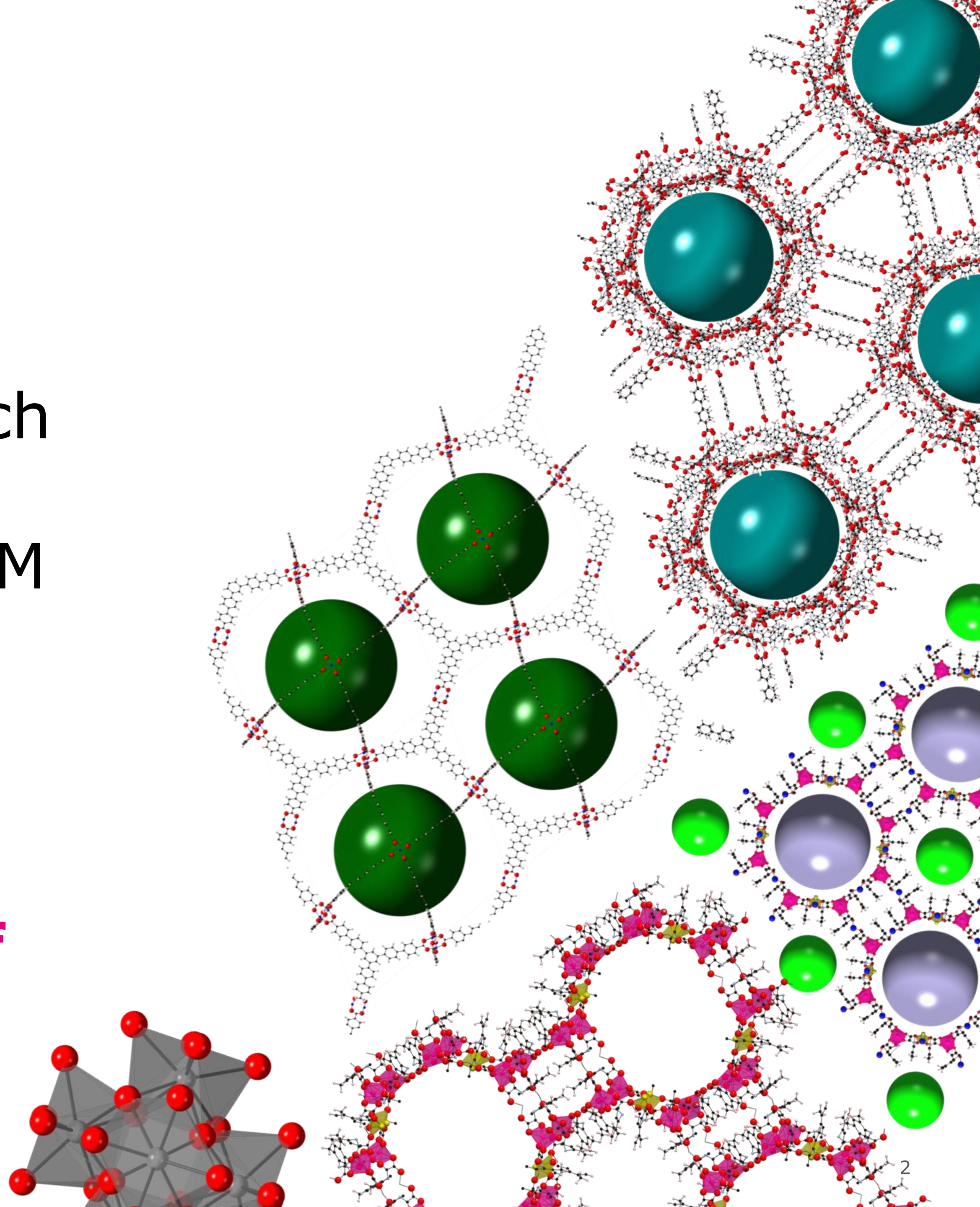
IWCCU 2021

16-02-2021

Agenda

- Who is JM?
- Our priorities for MOF research
- MOF scale-up case study at JM

Aim to give an overview of MOF scale up work at JM.



JM

A speciality chemicals company and a world leader in sustainable technologies

Over **200 years of history** dating back to 1817

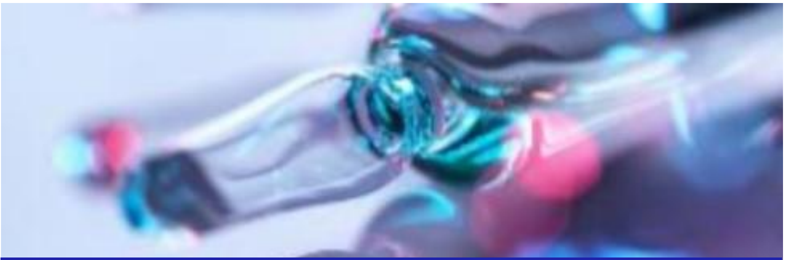
R&D Focused, with ~12% of employees working in R&D.

100+ PhDs funded by JM throughout world

JM

We serve global markets

Automotive



Pharmaceutical and medical

Chemicals

Oil and gas

Agrochemicals and fertilisers

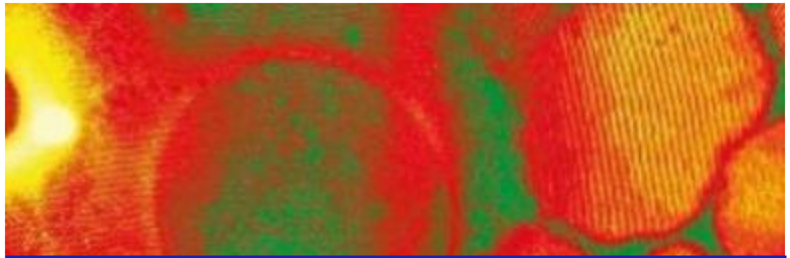
Food and beverage

Energy generation and storage

Glass

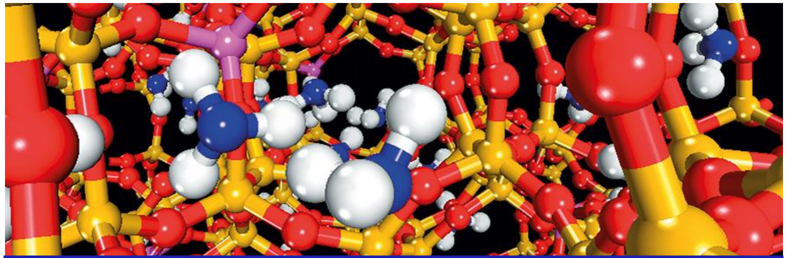
Other industrial

World class science and technology expertise

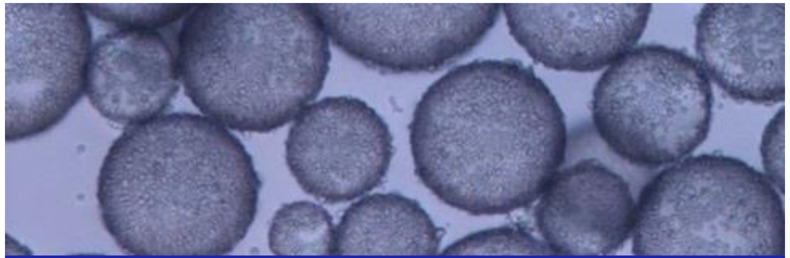


Characterisation and modelling

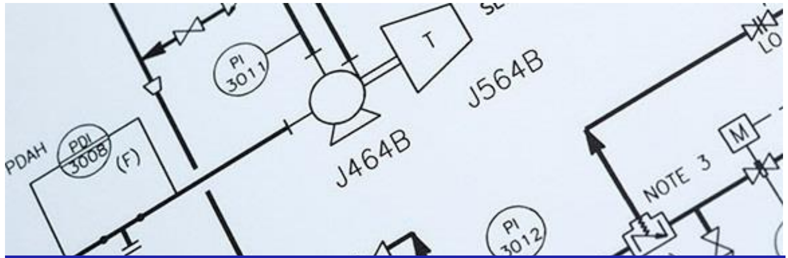
Chemical synthesis



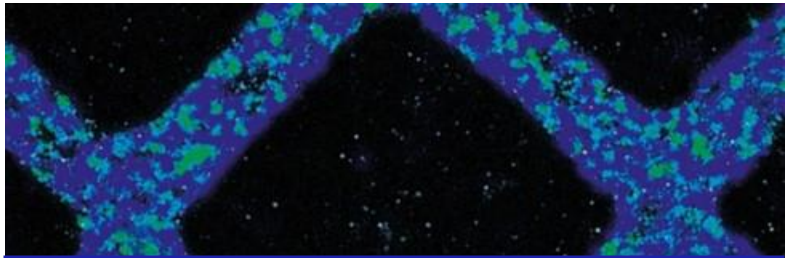
Material design and engineering



Product formulation



Process optimisation



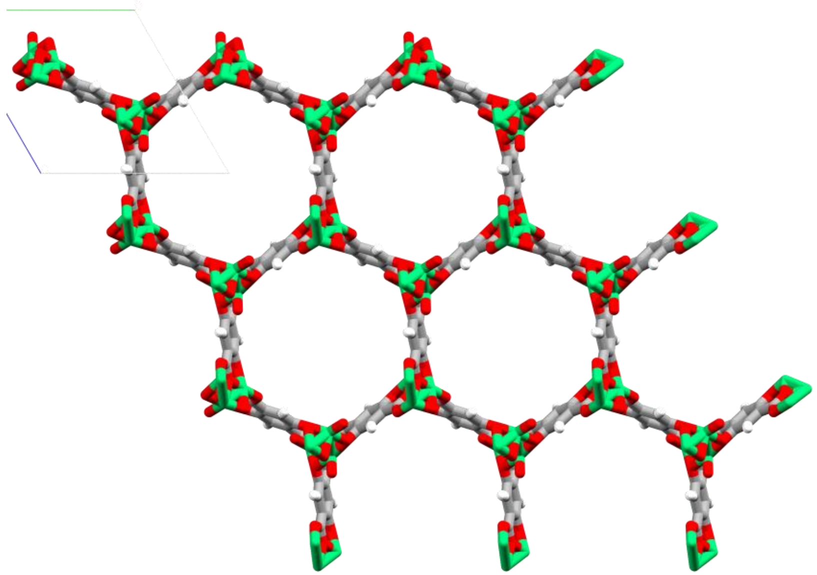
Surface chemistry and coatings

Pgm chemistry and metallurgy

Catalysis and advanced materials

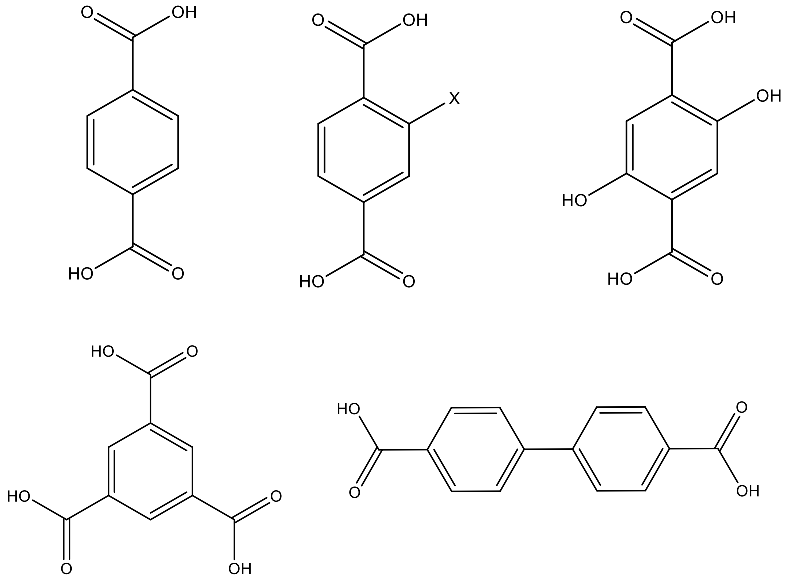
Electrochemistry

What are Metal-Organic Frameworks (MOFs)?



Functional hybrid materials consisting of metal nodes connected by organic linkers.

- **High surface areas**
  - 1 g of material possessing the same surface area as a football pitch
- Huge number of possible structures with ~70 k reported [1].
- Functionality arises from:
  - **Porosity**, **pore structure**, metal nodes & linker functional groups
- Certain MOFs are **stable under harsh conditions**
- Lots of academic interest over the last ~30 years
- Several products using MOFs now exist
  - TruPick™ & ION-X

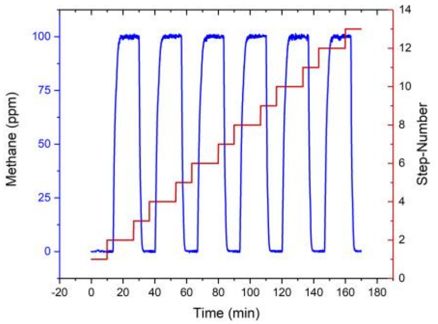


Need to develop large scale, cost effective scale-up routes to make these application a reality

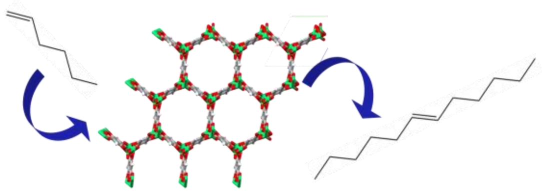
[1] P. Z. Moghadam, et al. Chem. Mater. 2017, 29, 2618−2625

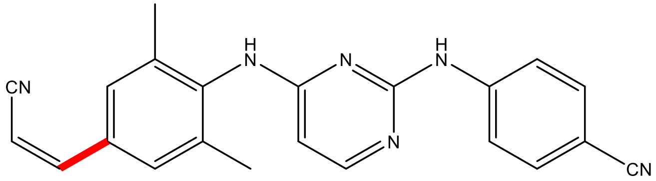
Current key priorities in JM MOF work

Separations and purification

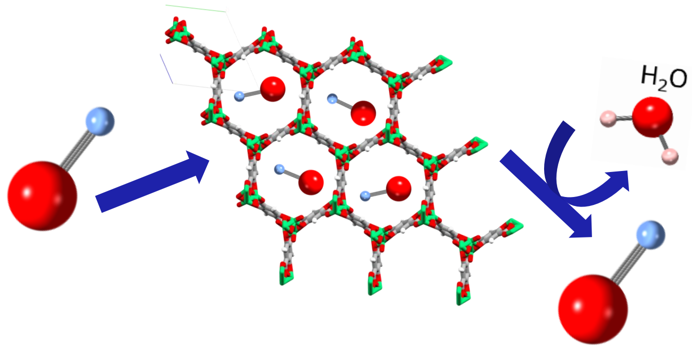


Fine Chemical Catalysis



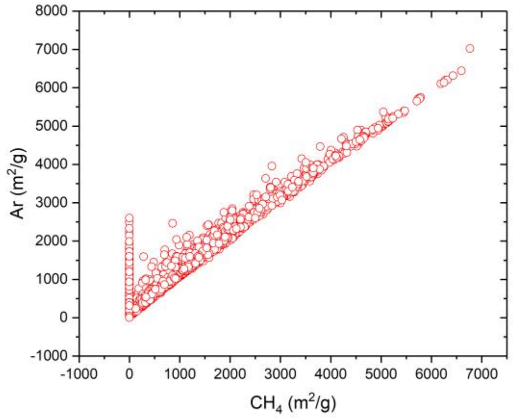


Controlled release

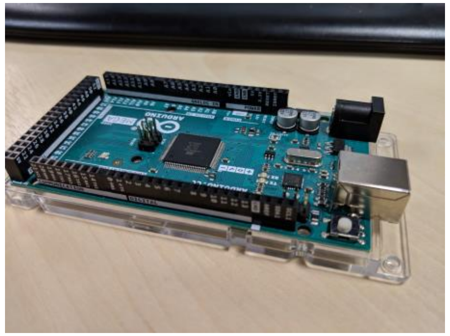


Forming and scale-up

Modelling

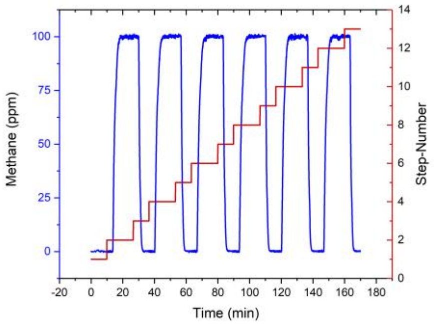


In-situ monitoring

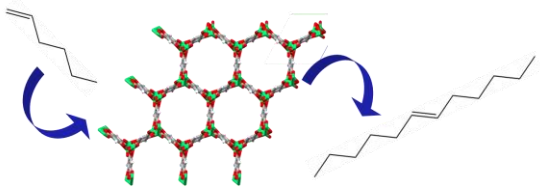


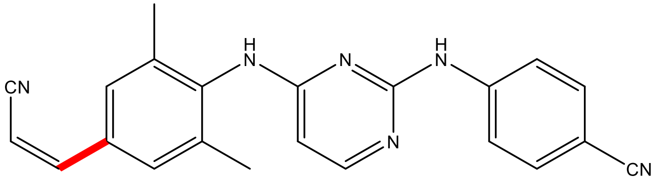
Current key priorities in JM MOF work

Separations and purification

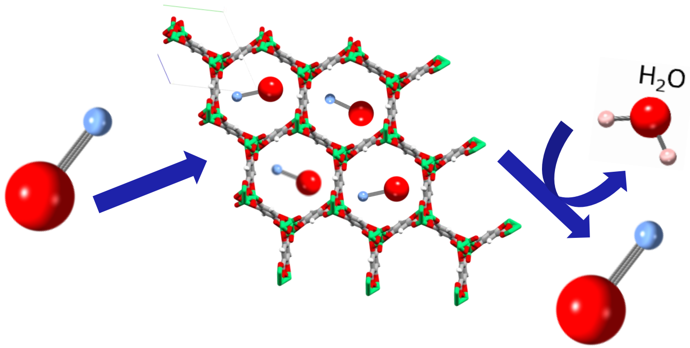


Fine Chemical Catalysis



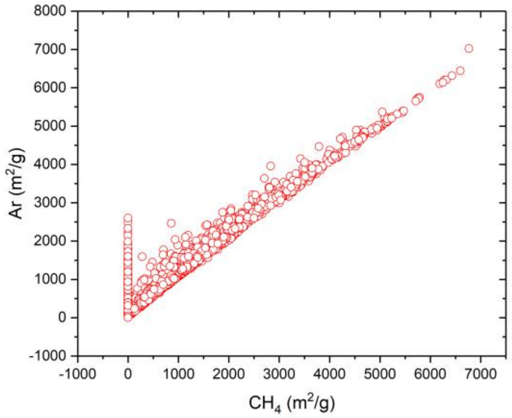


Controlled release

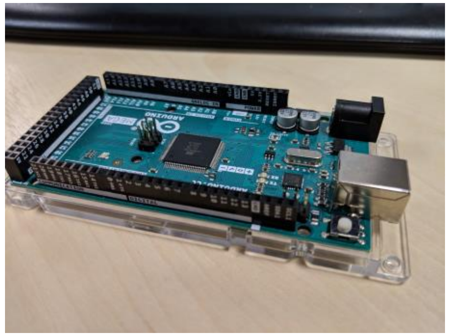


Forming and scale-up

Modelling



In-situ monitoring



Scale-up considerations

Chemical

- Concentration
- Temperature
- Solvent

Physical

- Mixing
- Separation
- Washing
- Waste
- Product performance

Solvent	Safety Score	Health Score	Env. Score	Ranking
H_2O	1	1	1	Recommended
EtOH	4	3	3	Recommended
MeOH	4	7	5	Problematic
THF	6	7	5	Problematic
DMF	3	9	5	Hazardous
Sulfolane	1	9	7	Hazardous

D. Prat, et al., *Green Chem.*, 2016, **18**, 288-296

Reduction of raw materials is key for MOF scale-up

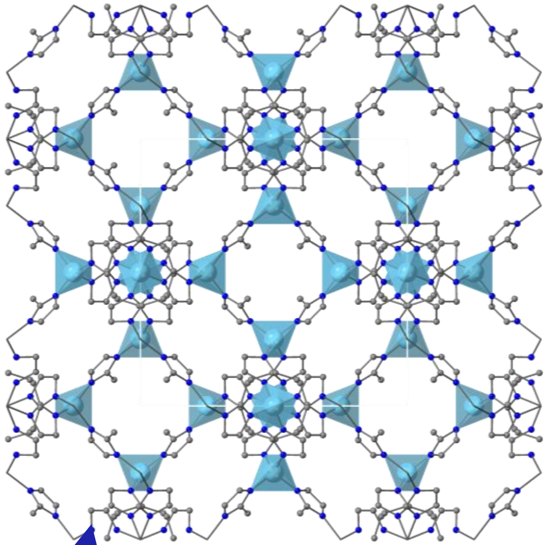
JM

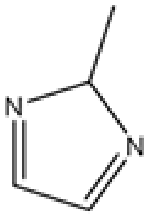
Nano ZIF-8 scale-up case study

Properties
- Very high surface area ~ 1600 m^2g^{-1}
- High thermal stability – stable 400 ^oC
- Pore aperture – 3.4 Å

Application
- Used in pre-combustion application - separation of H_2/CO_2
- Nano sized needed for membrane applications

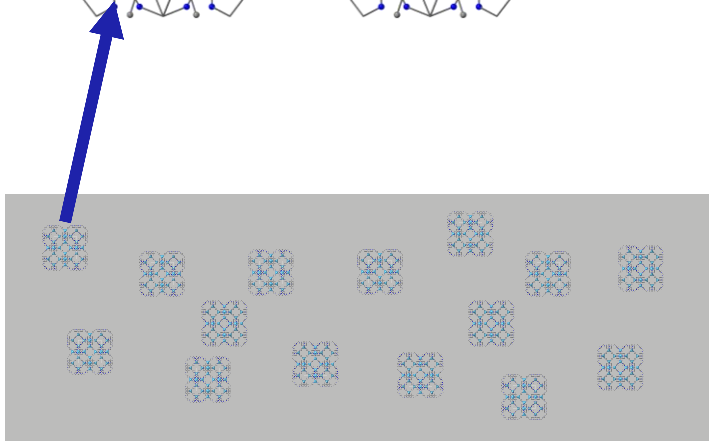
ZIF-8





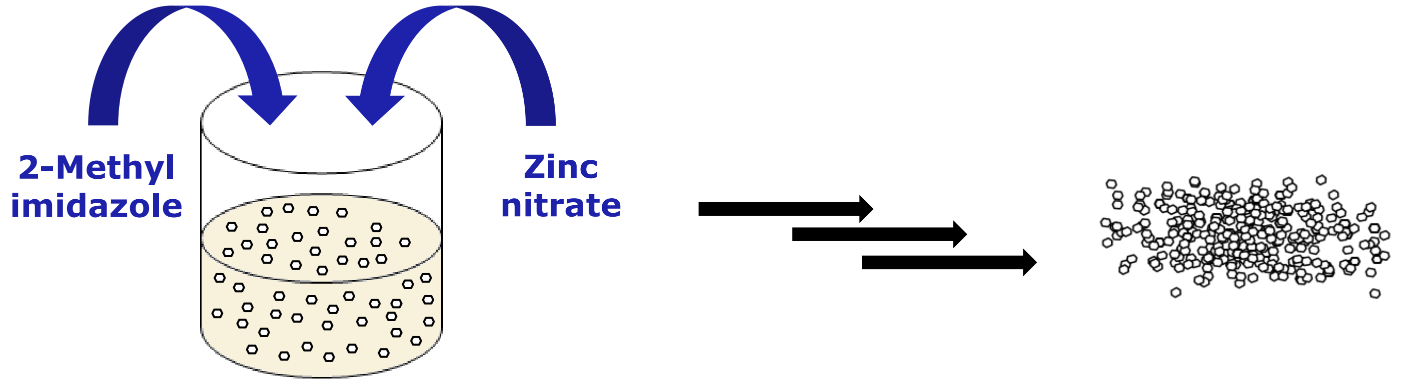
2-Methylimidazole

Zn^{2+} Zinc nitrate

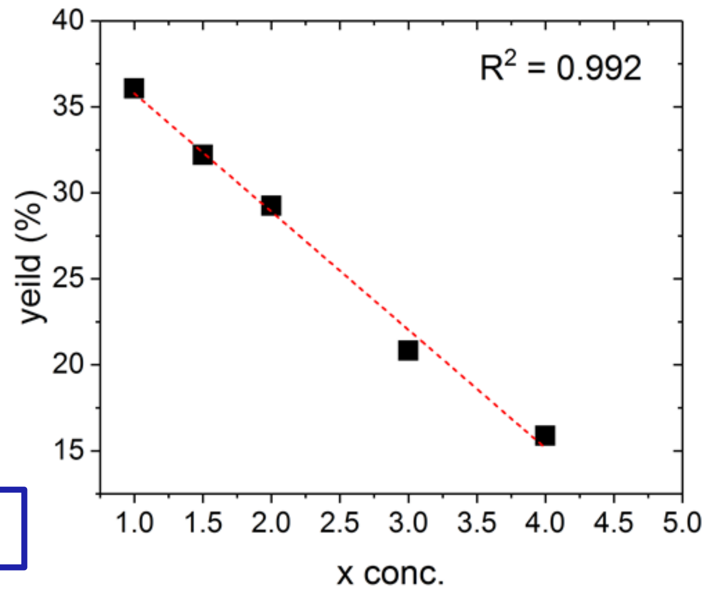


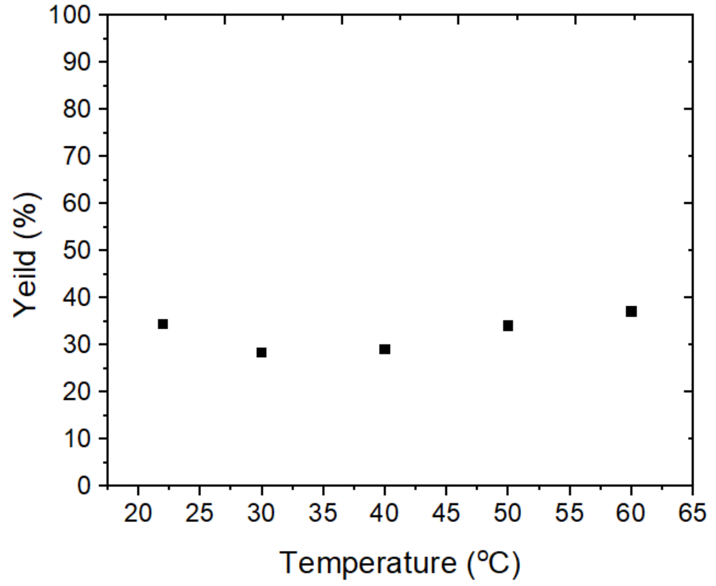
Mixed matrix membrane

Original nano ZIF-8 route



$$Zn(NO_3)_2.6H_2O + 2C_4H_6N_2 \rightarrow Zn(C_4H_5N_2)_2 + 2H^+ + 2NO_3^- + 6H_2O$$





- Dilute conditions needed
  - Large quantities of Methanol used ~ 5 L MeOH needed for 5 g of nano ZIF-8

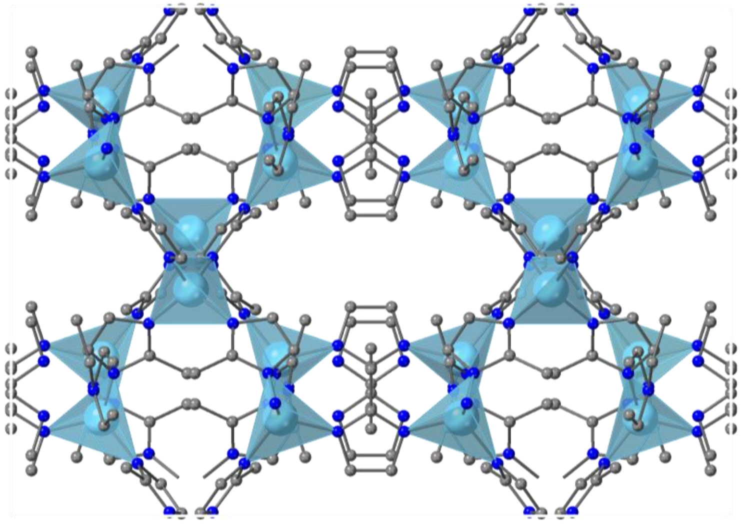
Parameter study showed its difficult to improve the original synthesis.

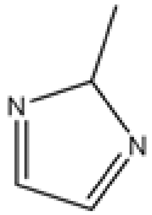
JM

ZIF-L as an alternative route to nano ZIF-8

Properties

- ZIF-L is a dense phase polymorph of ZIF-8
- Consists of same raw materials as ZIF-8
- 2D material connected by linker molecules – leaf shape
- Low porosity – 92 m^2g^{-1}

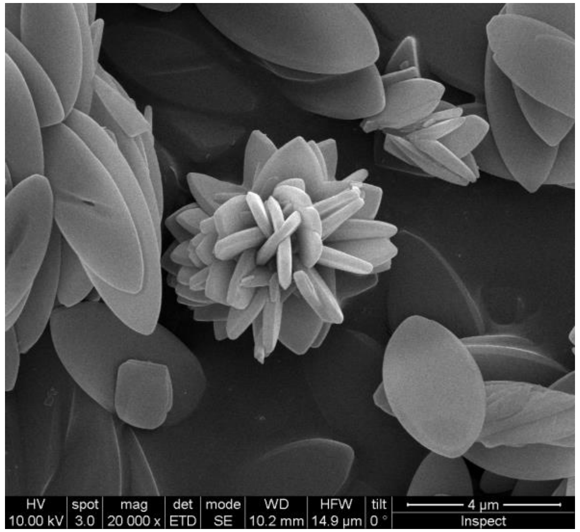




2-Methylimidazole

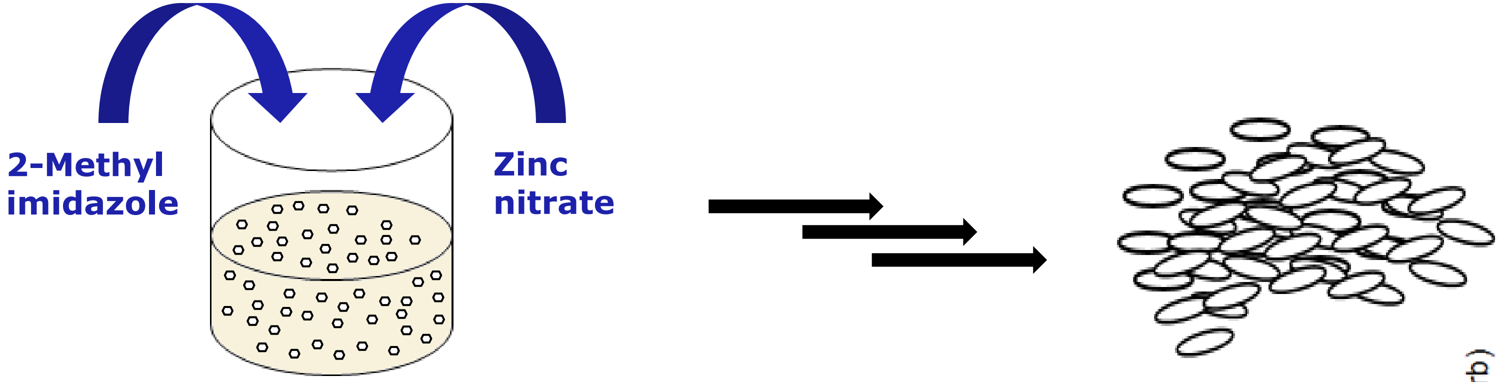
Zn^{2+} Zinc nitrate

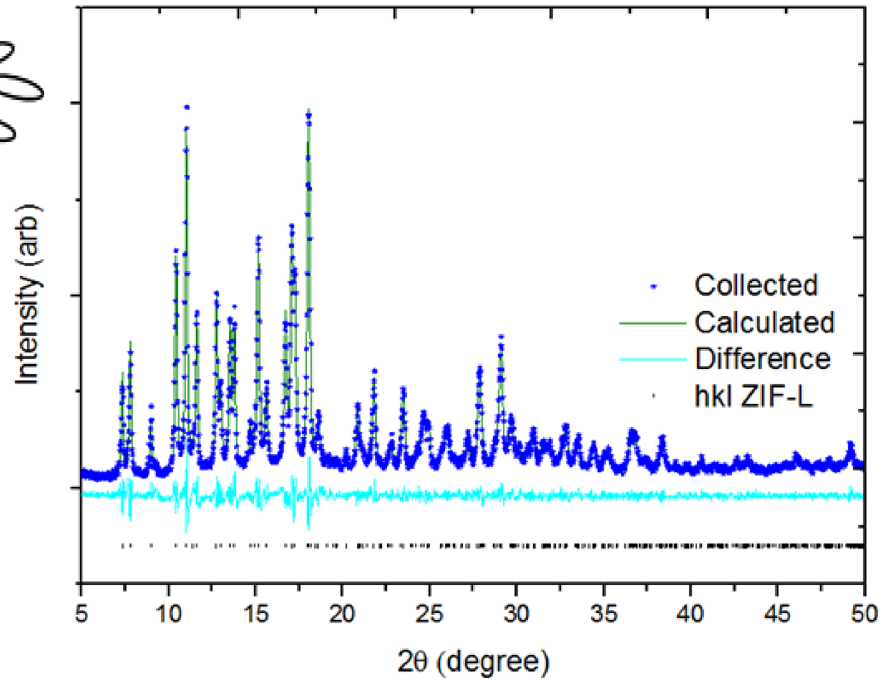
ZIF-L



JM

ZIF-L as an alternative route to nano ZIF-8

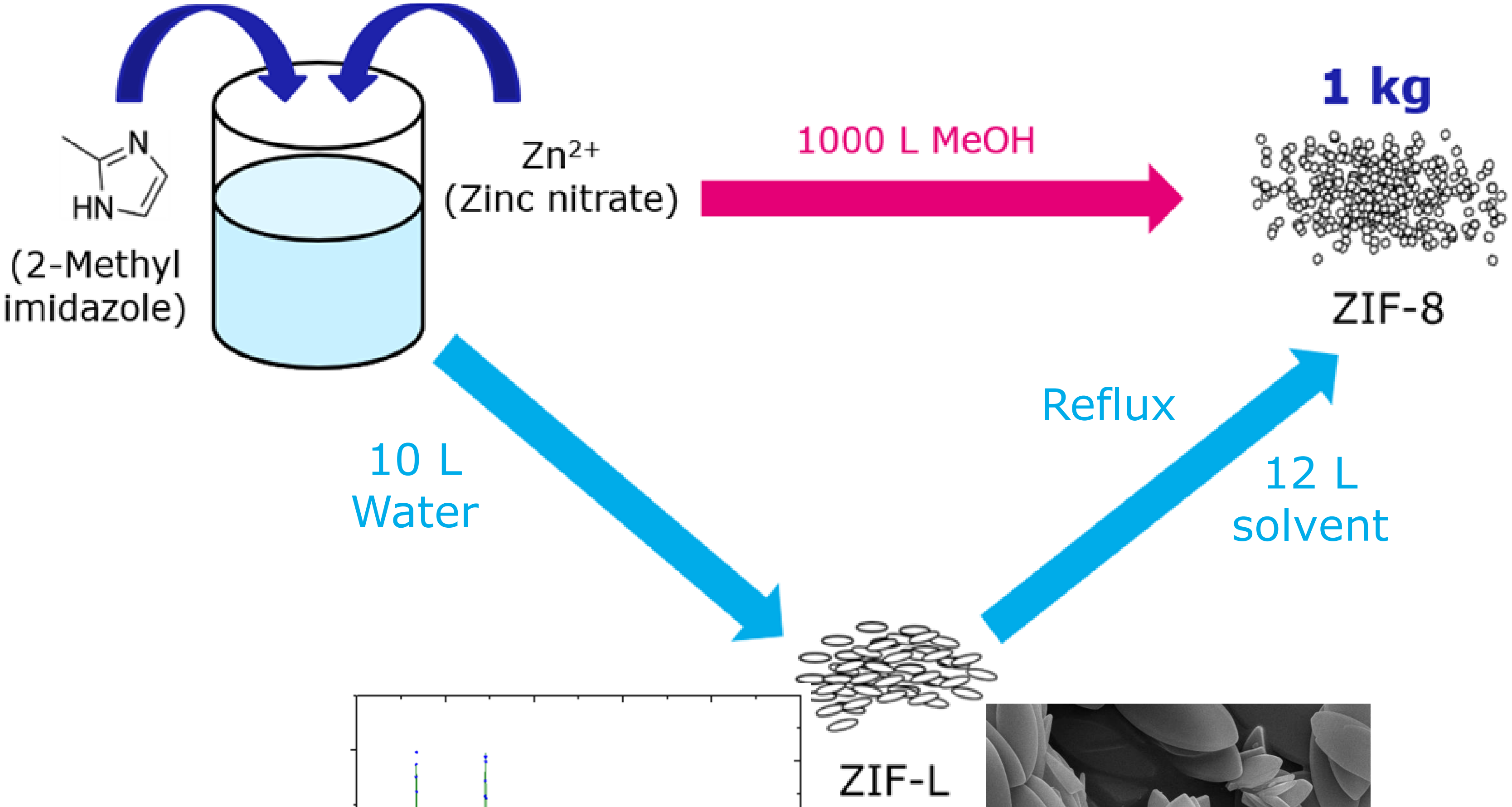


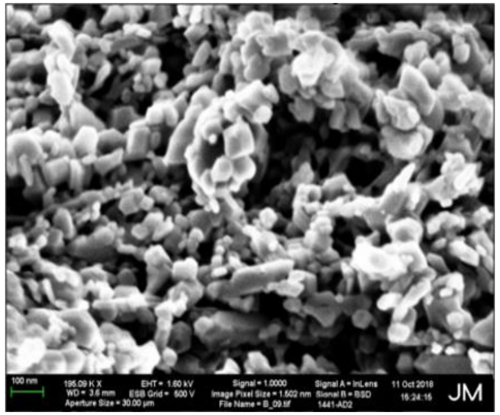


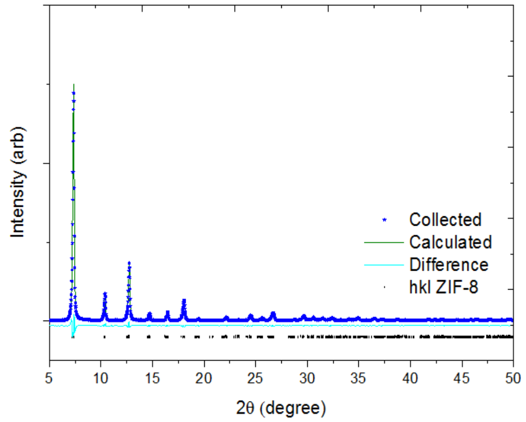
- Simple synthesis in water
- Concentrated reaction
- High yield ~ 90 %

JM

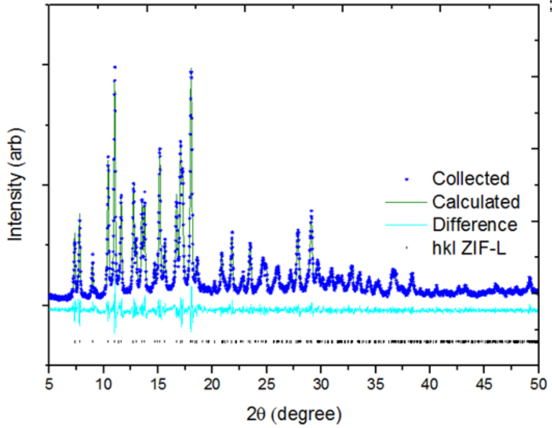
ZIF-L as an alternative route to nano ZIF-8

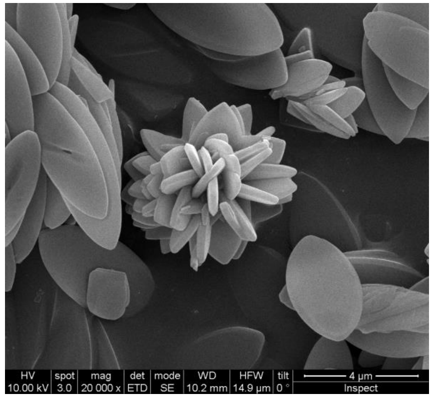






ZIF-8 BET surface area ~1600 m^2g^{-1}



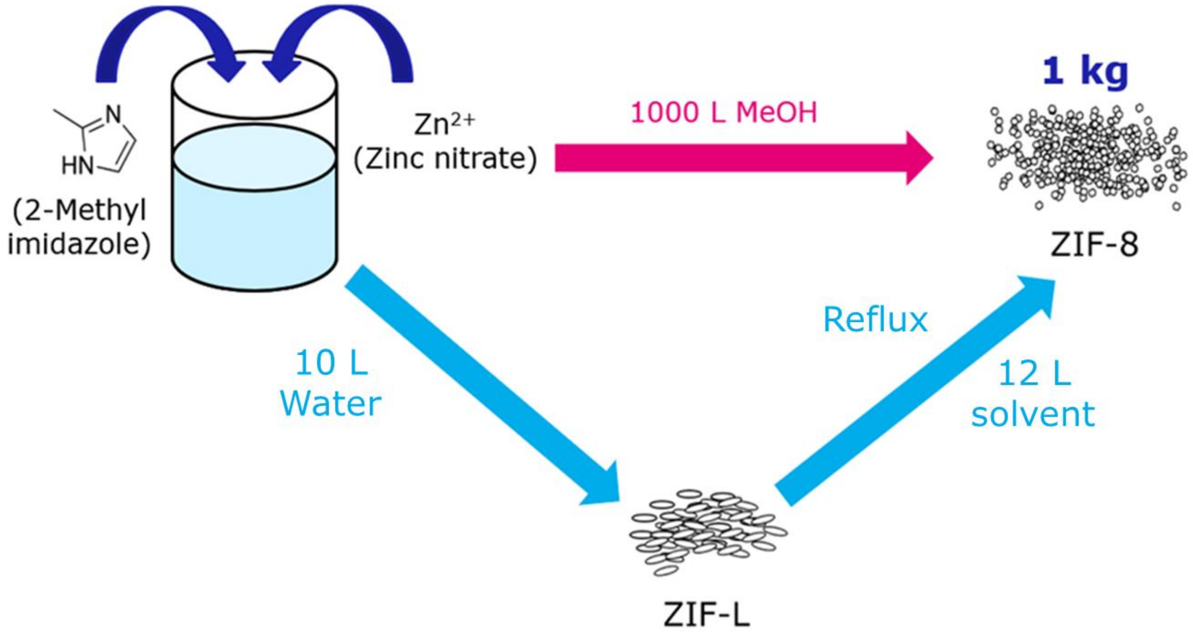


ZIF-L BET surface area 92 m^2g^{-1}

Nano-ZIF-8 case study summary

Developed scalable route

- Two order of magnitude solvent reduction
- Doubled overall all yield of nano-ZIF-8 synthesis
- Replaced methanol with non-toxic solvent
- Industrial scale concept for nano ZIF-8 designed.



7x reduction in cost to produce

JM

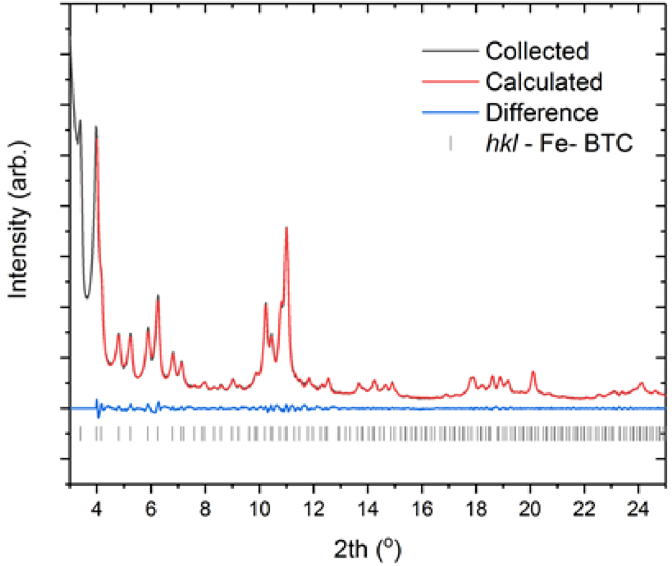
Other scale-up examples

Scale-up: Fe-BTC

- 60 L batch reaction vessel
- Washed in purpose built setup
- 15 kg MOF produced
- BET surface area ~1500 m^2/g

Scale-up: CPO-27-Ni

- 10 kg CPO-27-Ni
- Used in heat pump and desalination demonstrator unit in Egypt



ProDIA

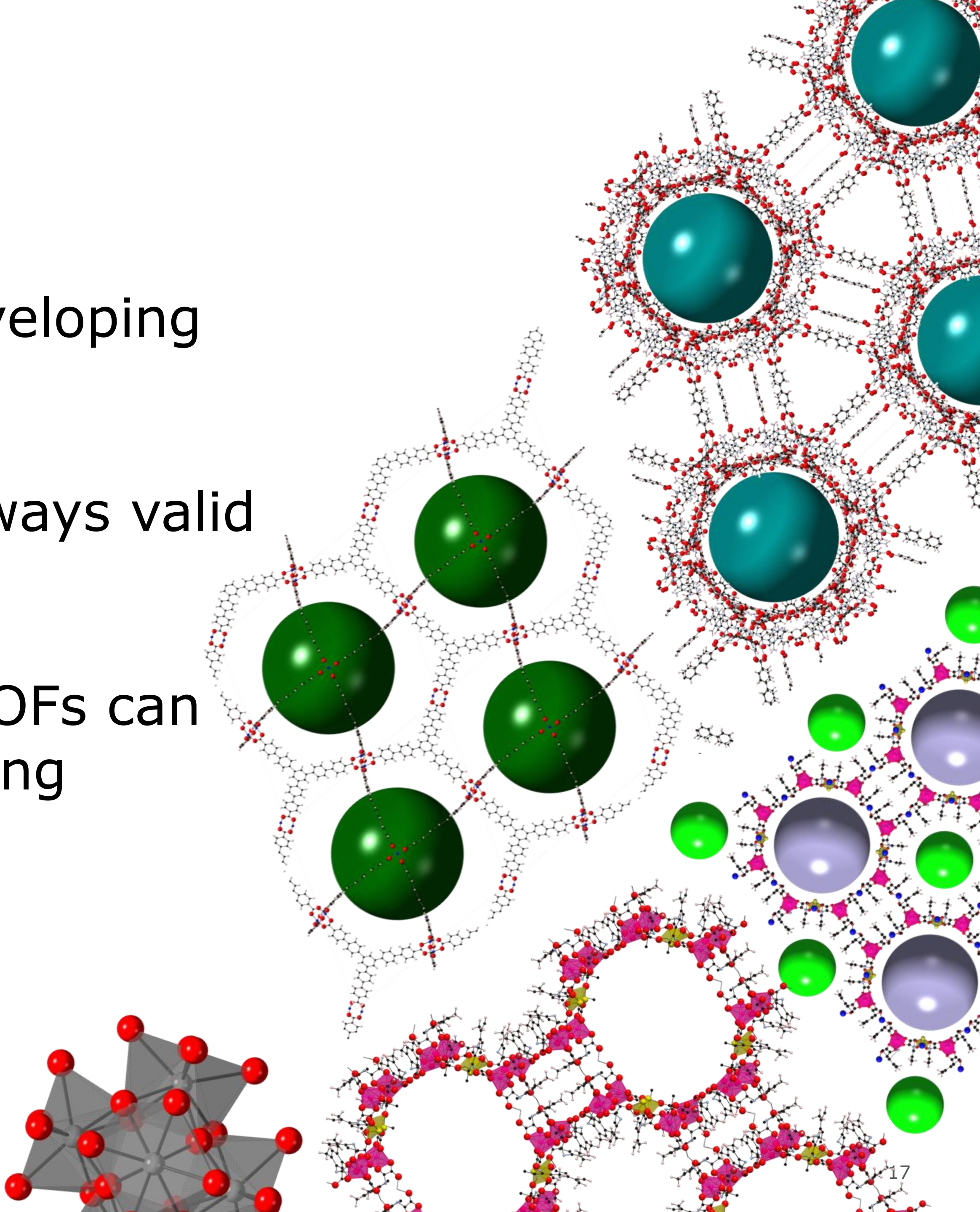
JM

Summary

- Reducing raw materials cost key to developing large scale synthesis

- Conventional scale-up methods not always valid
  - Chemistry of MOFs is important

- Commercial large scale synthesis of MOFs can be achieved with the right understanding



JM

Acknowledgments

JM

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Catalyst Research Group – Chilton

UNIZAR

Joaquin Coronas

Magdalena Malankowska

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WE
CAN DO
SO MUCH
TOGETHER

INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILIZATION
TU/E - EINDHOVEN - 16-17 FEBRUARY 2021

PBI based mixed matrix hollow fiber membranes for pre-combustion CO_2 capture

Dr Miren Etxeberria Benavides
TECNALIA

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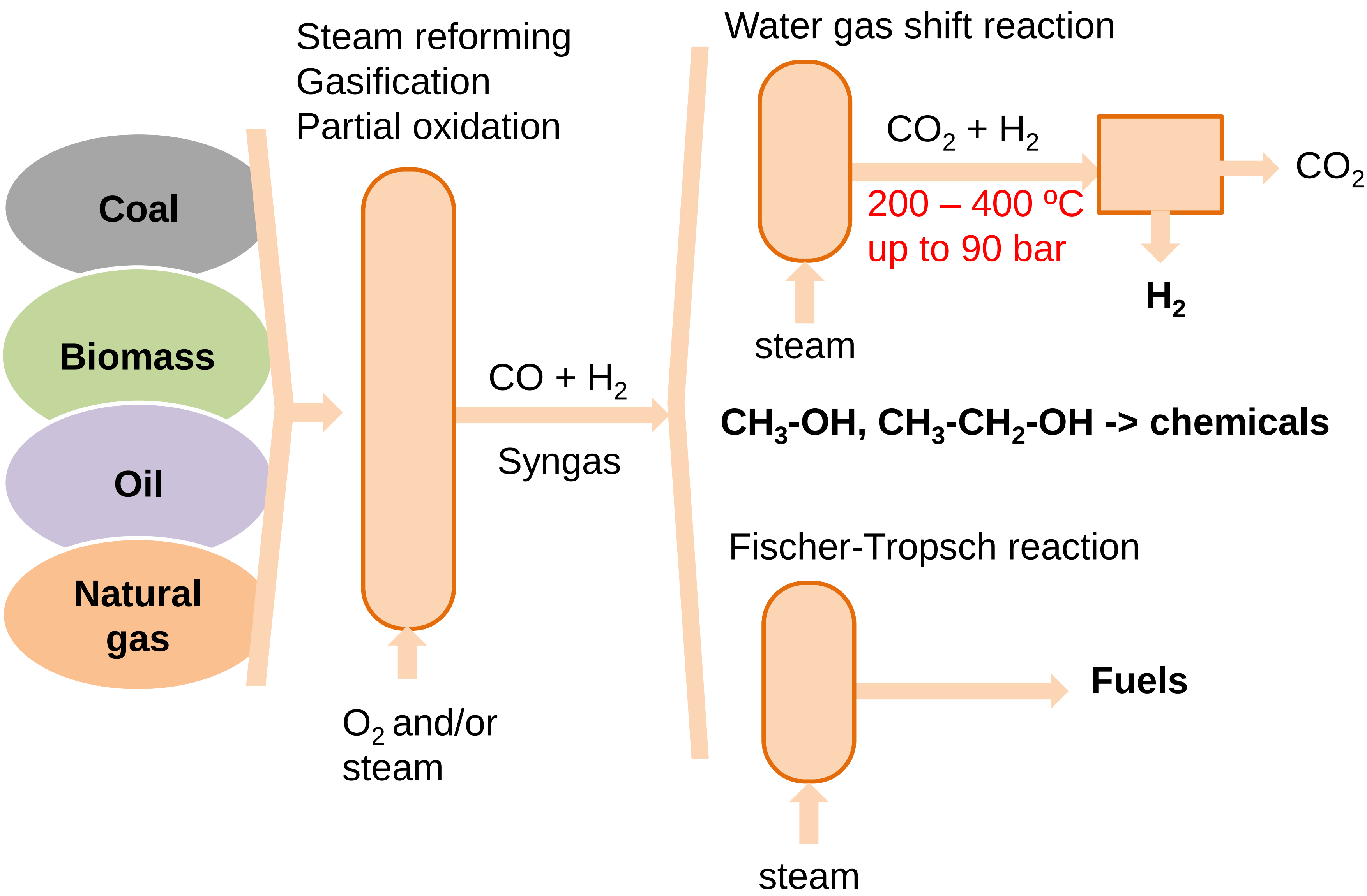
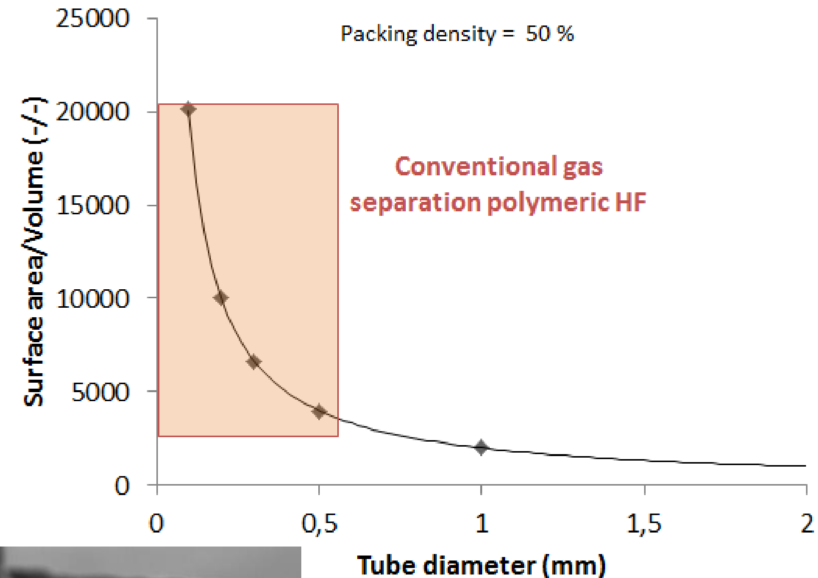
DSSINNOVA 2016

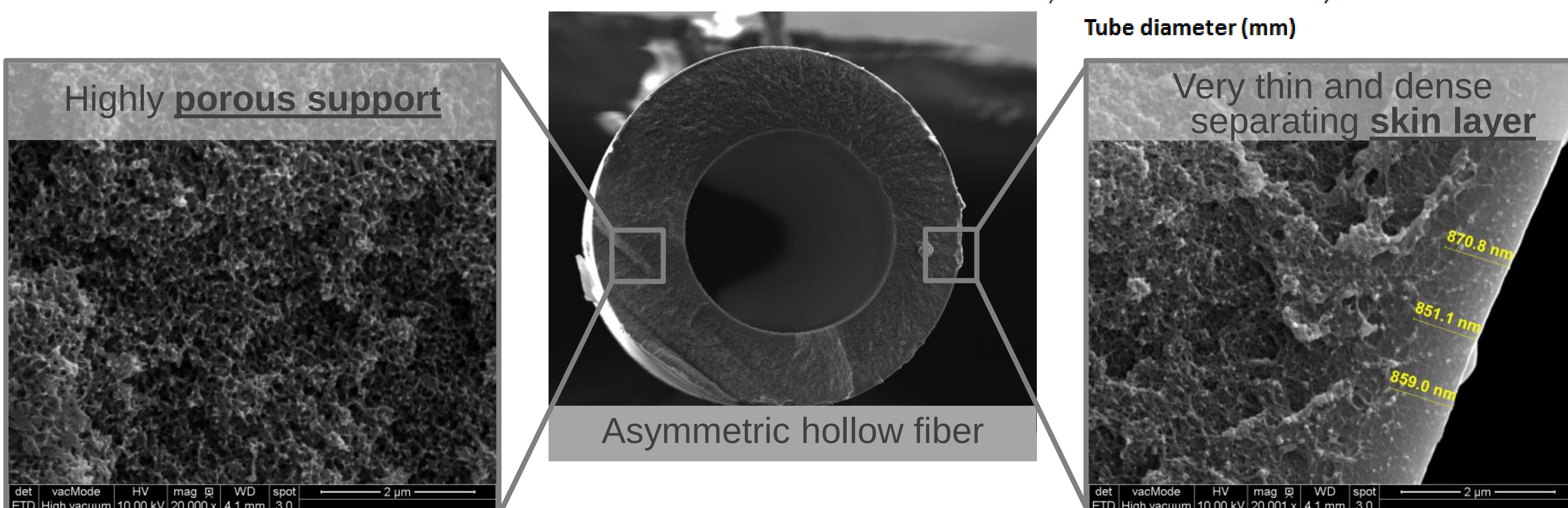
Pre-combustion CO_2 capture

Chemical transformations before combustion = pre-combustion carbon capture

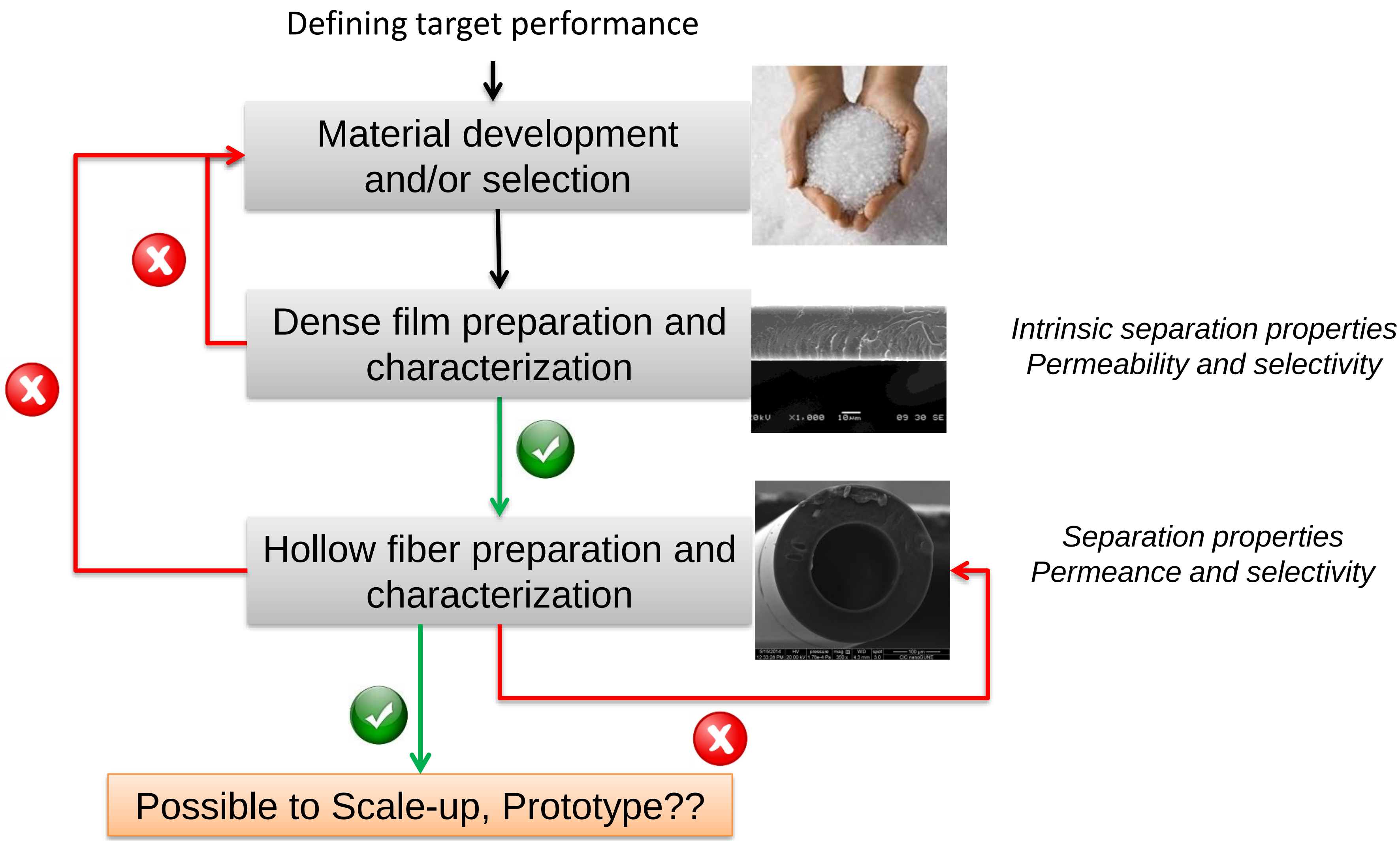


HOLLOW FIBER MEMBRANES



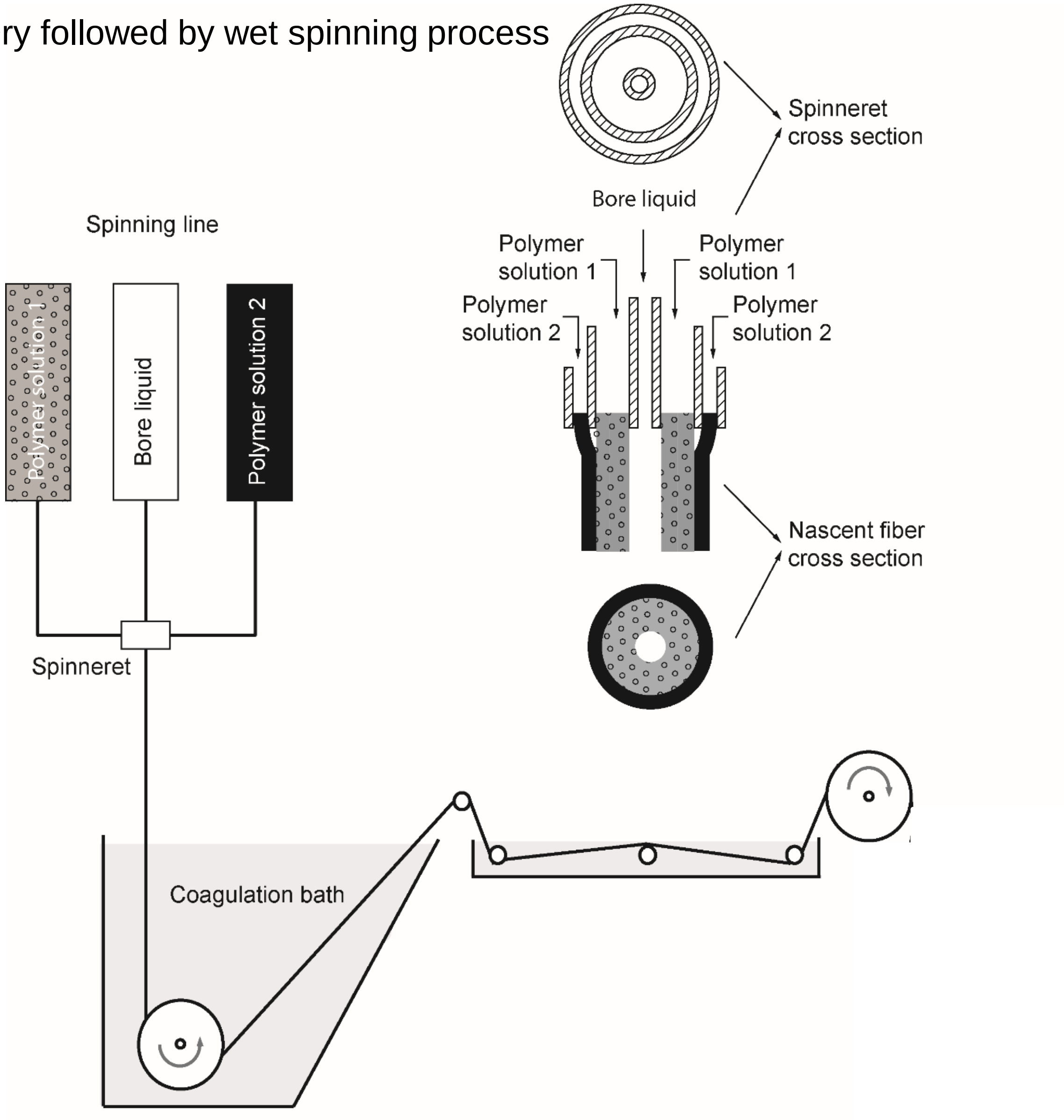


Membrane Development Strategy



HOLLOW FIBER SPINNING

Dry followed by wet spinning process



Process parameters

Dope Composition

Dope Flow rate

Bore Composition

Bore Flow Rate

Spinning Temp

Coagulation Bath Temp

Air Gap height

Take-up rate

Room T

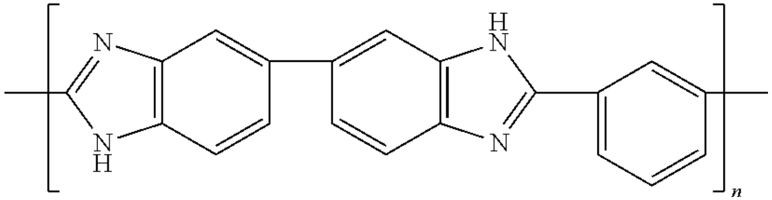
Humidity

M^4CO_2 project

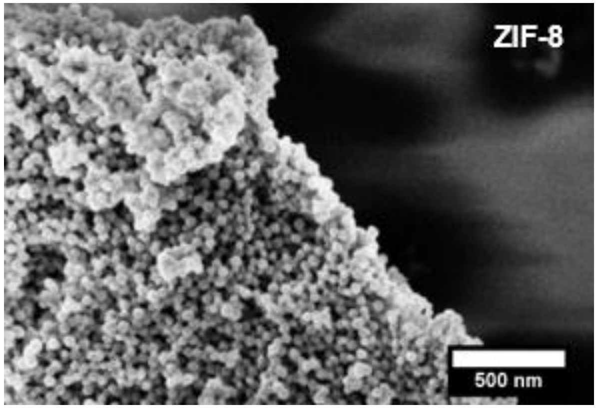
The M^4CO_2 project aims at developing and prototyping Mixed Matrix Membranes based on highly engineered Metal organic frameworks and polymers (M4) for energy efficient CO_2 capture in power plants and other energy-intensive industries both for pre-combustion and post combustion applications

PBI Asymmetric hollow fiber

Tg 420ºC



Filler: ZIF-8 powder



Particle size ~ <60 nm

Kinetic diameter (Å)	
H_2	2.89
CO_2	3.3

https://doi.org/10.1016/j.seppur.2019.116347

H_2/CO_2 separation performance at 150ºC

Single gas test (SG)

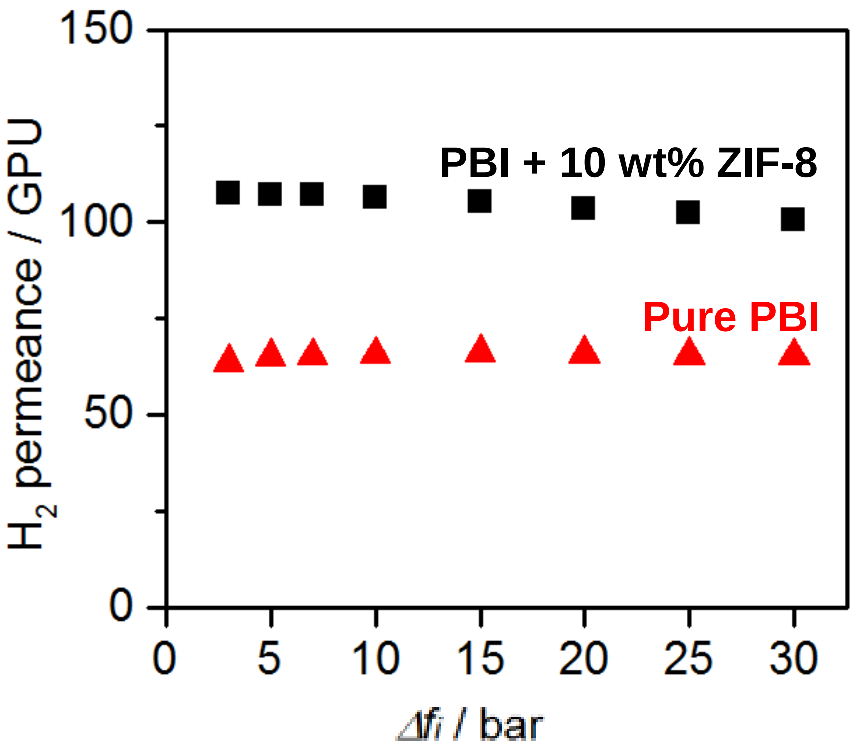
Pure PBI

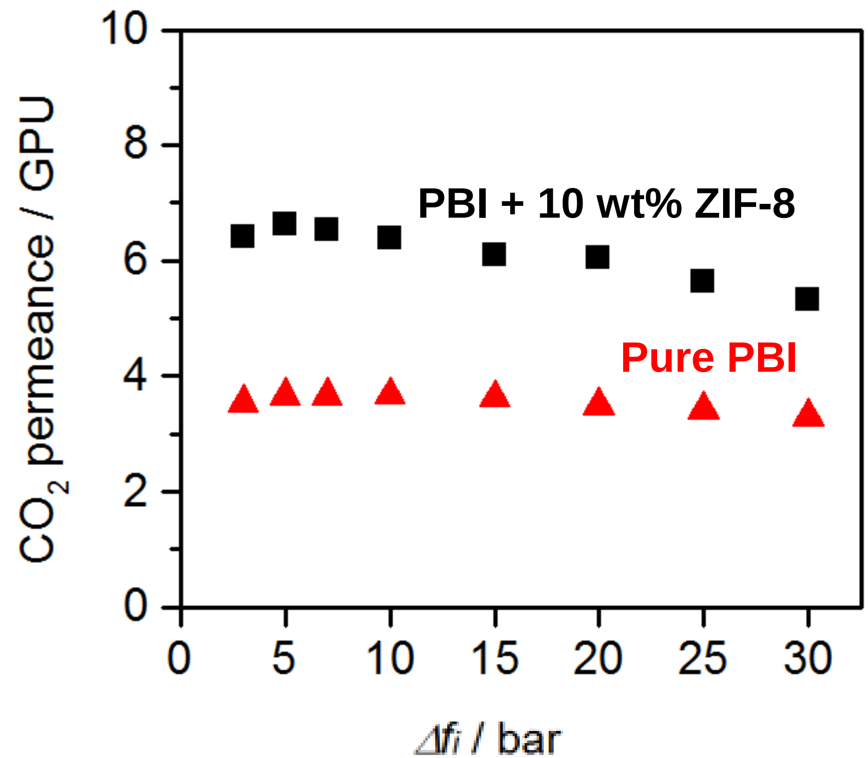
63 GPU H_2; 17.8 H_2/CO_2

vs

PBI + 10 wt% ZIF-8

107 GPU H_2; 16.6 H_2/CO_2





Dense PBI film
20 Barrer H_2; 20 H_2/CO_2

Journal of MembraneScience 461 (2014) 59–68

H_2/CO_2 separation performance at 150ºC

Single gas test (SG)

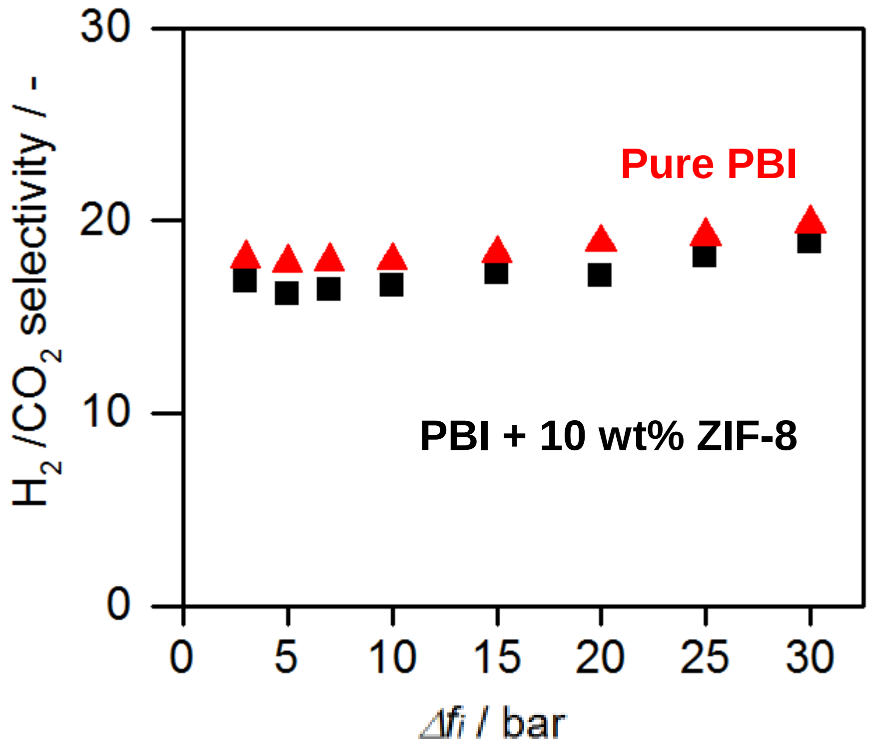
Pure PBI

63 GPU H_2; 17.8 H_2/CO_2

vs

PBI + 10 wt% ZIF-8

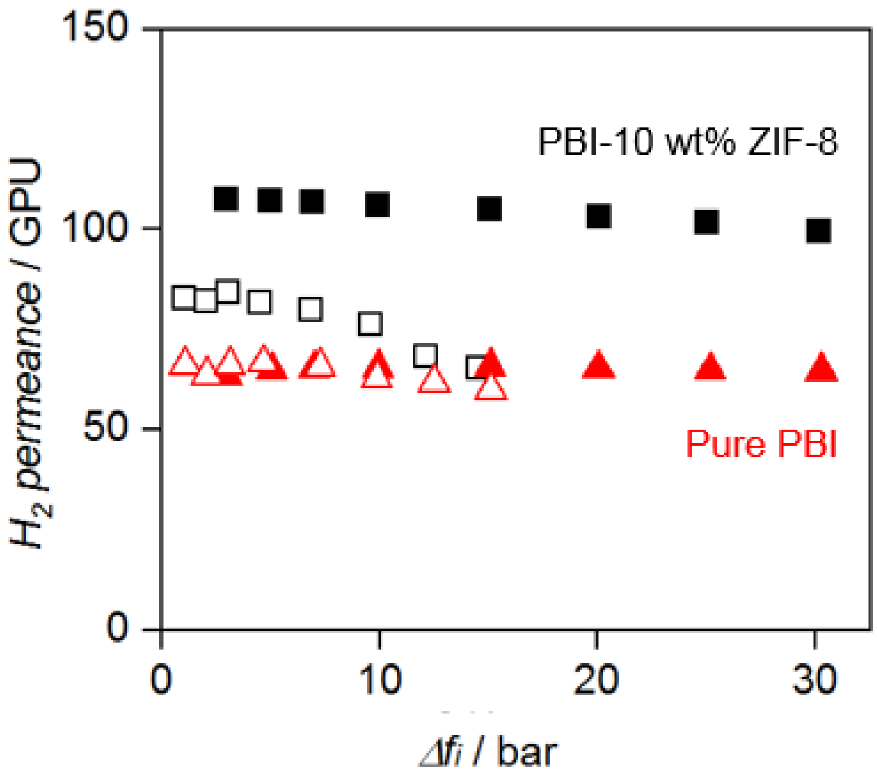
107 GPU H_2; 16.6 H_2/CO_2

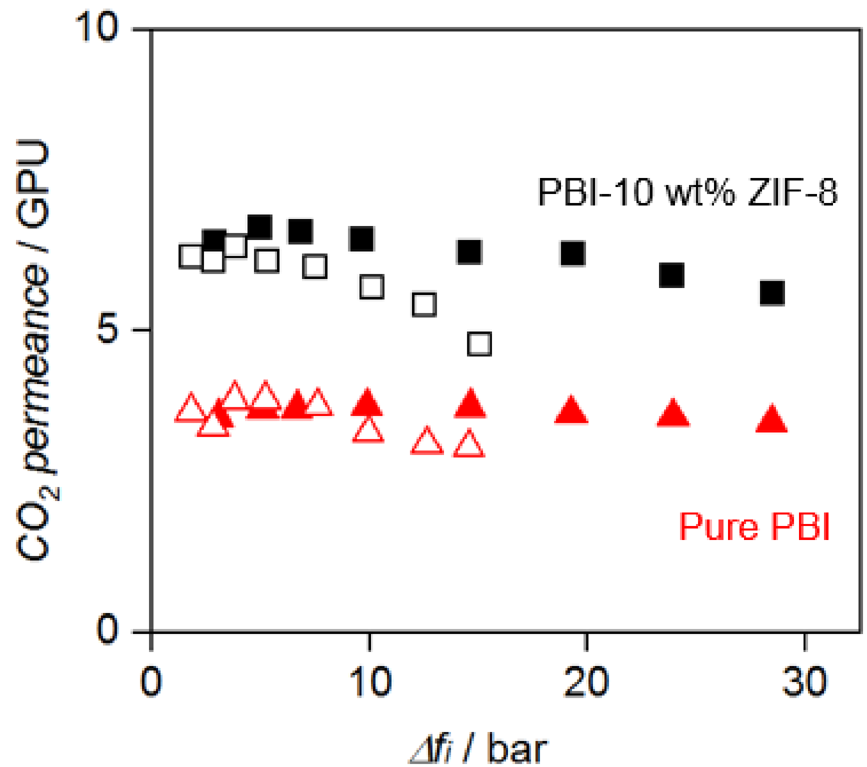


H_2/CO_2 separation performance at 150ºC

Single gas test vs *Mixed gas test (50/50 H_2/CO_2)*

(closed symbols) *(open symbols)*



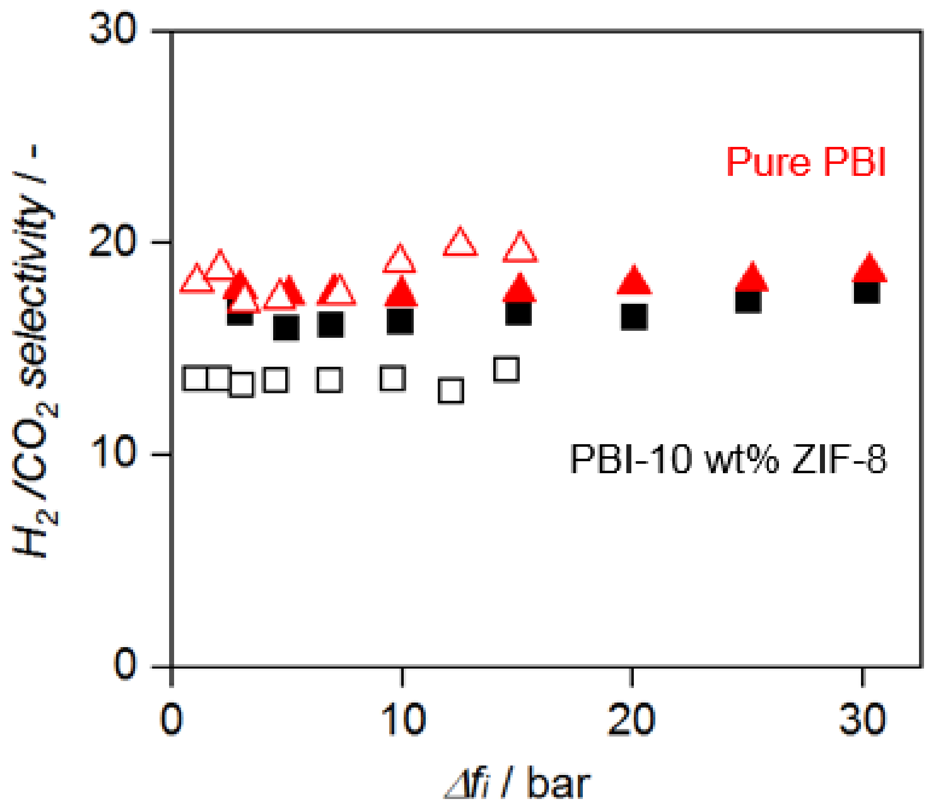


H_2/CO_2 separation performance at 150ºC

Single gas test
(closed symbols)

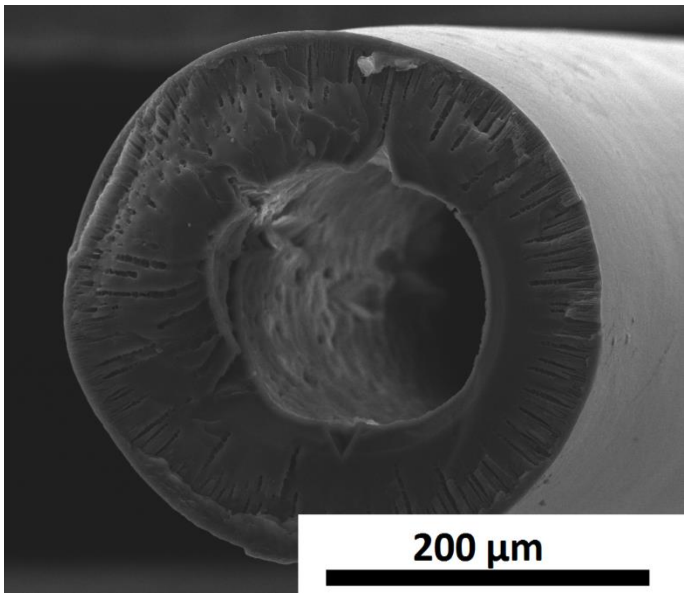
vs

Mixed gas test (50/50 H_2/CO_2)
(open symbols)



M^4CO_2 project

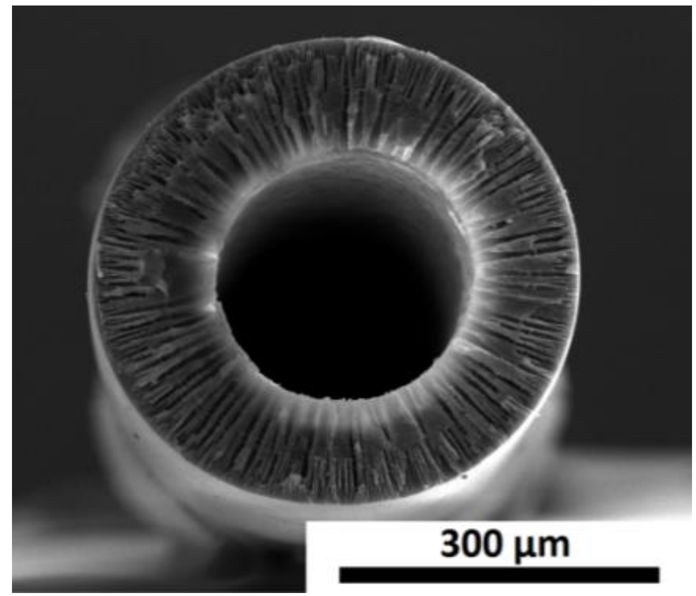
Pure PBI



Maximum take up rate: 20 m/min

OD/ID: 370 µm / 160 µm

PBI + 10 wt% ZIF-8



Maximum take up rate: 14 m/min

OD/ID: 470 µm / 250 µm

Mechanical stability (Mandrel test)

MEMBER project

The key objective of the MEMBER Project is the **scale-up and manufacturing of advanced materials** (membrane and sorbents) and their demostration at industrially relevant conditions in novel membrane based technologies that outperform current technologies for pre- and post-combustion CO_2 capture in power plants as well as H_2 generation with integrated CO_2 capture

Prototype A	Prototype B	Prototype C
Pre-combustion CO_2 capture	Post-combustion CO_2 capture	Pure H_2 production with integrated CO_2 capture
MMM hollow fiber membranes	MMM hollow fiber membranes	Pd-based membranes

MEMBER project

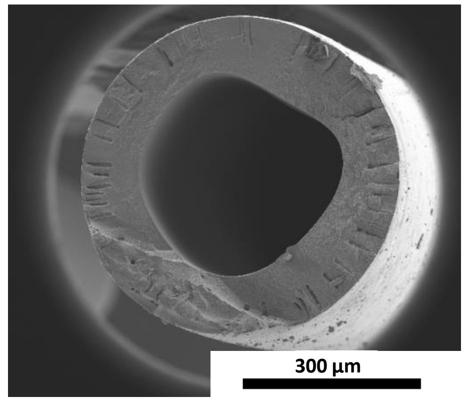
Objectives for PBI based membrane scaling up:

- Increase production rate (take-up rate)
- Decrease fiber dimensions
- Improve mechanical properties

MEMBER project

PBI

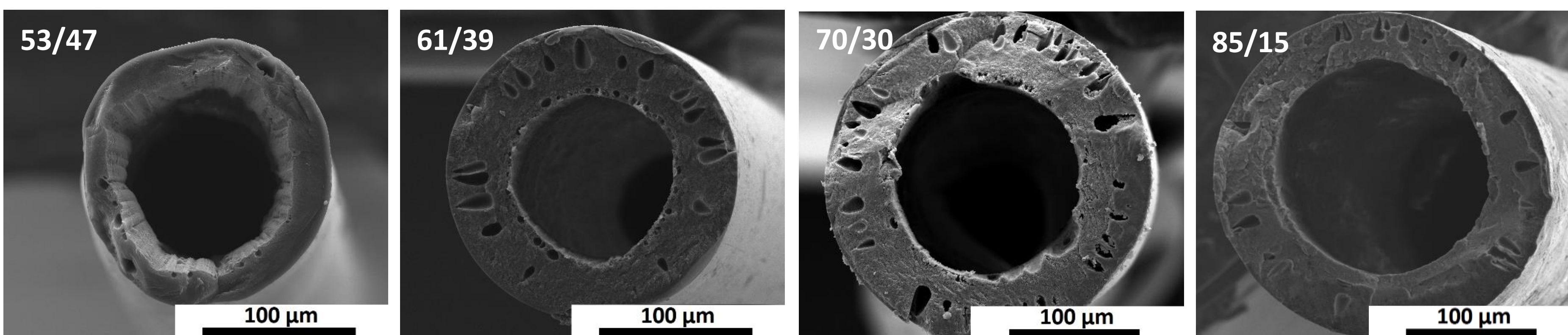
Take up rate: 6 m/min



540 µm / 340 µm

PBI/PVP

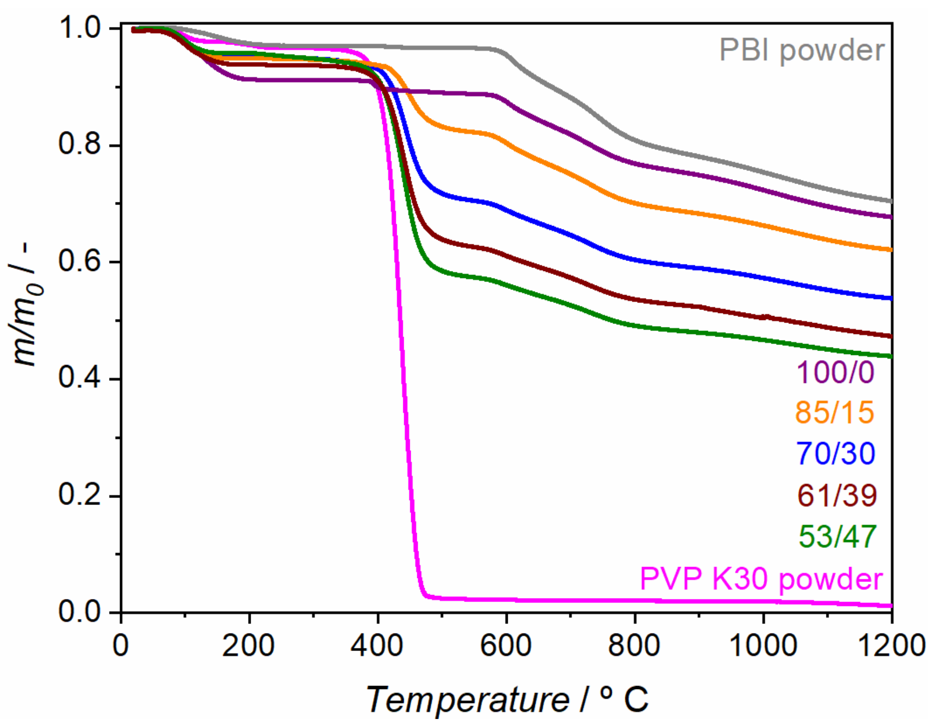
Take up rate: 25-50 m/min



175 µm / 115 µm *195 µm / 110 µm* *275 µm / 165 µm* *270 µm / 175 µm*

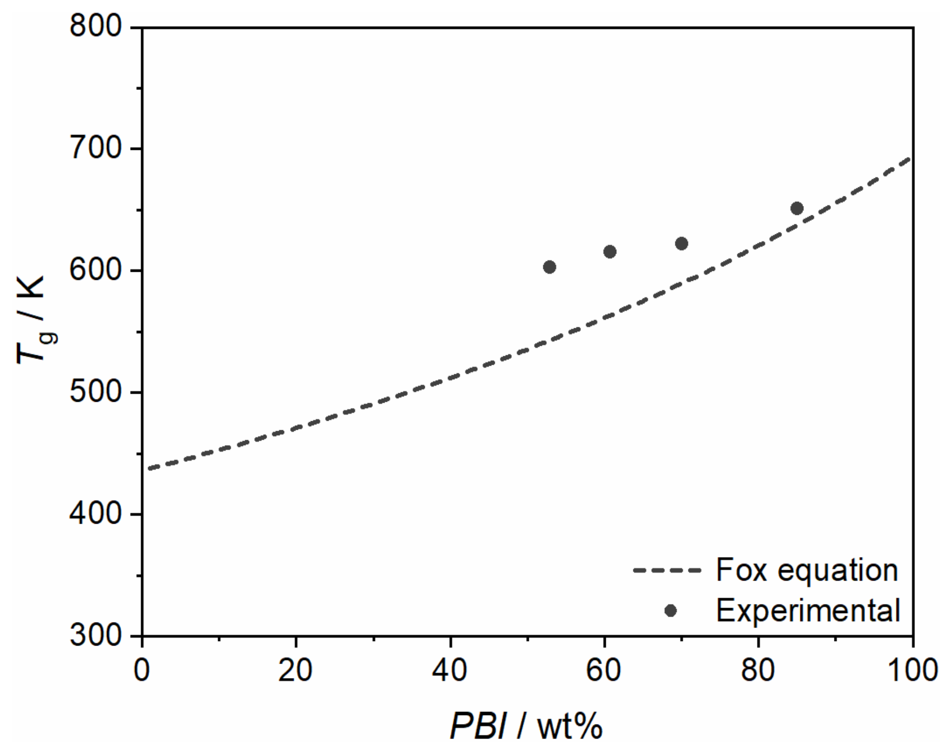
PBI/PVP blend fibers

TGA



Thermally stable up to ~340 °C

DSC



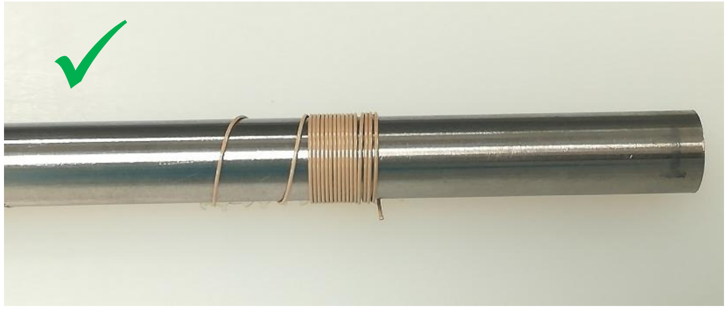
Hydrogen bonds between the N-H group of PBI and the C=O group of PVP

H_2/CO_2 separation performance at 150ºC

Mixed gas test (50/50 H_2/CO_2)

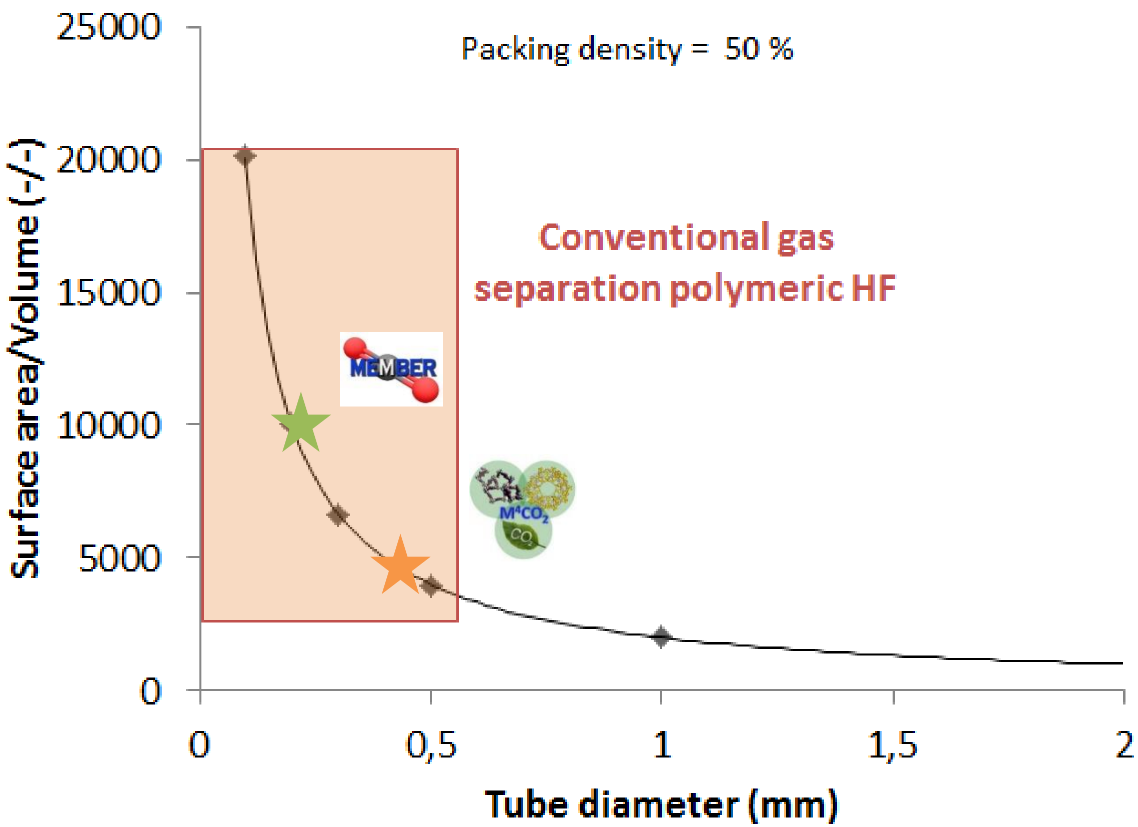
	H_2 Permeance (GPU)	H_2/CO_2 Selectivity (-)	OD/ID (µm)	Take up rate (m/min)	Defect heling treatment (PDMS)
PBI/PVP	56	16.6	275/165	25	No
10 wt% ZIF-8	121	10.2	290/175	25	Yes
5 wt% ZIF-8	31	17	270/175	25	No

Mechanical stability (Mandrel test)



M^4CO_2 project vs MEMBER project

	Take up rate	Fiber diameter	Surface area/volume	PDMS coating	Mechanical stability (mandrel test)	PBI quantity required for m^2 of fiber
	14 m/min	470 μm	~ 5000	Yes	✗	~30 g PBI / m^2
	25 m/min	270 μm	~ 10000	No	✓	~15 g PBI / m^2



Conclusions

- PBI/ZIF-8 mixed matrix hollow fiber membranes:
  - ZIF-8 incorporation into the PBI polymer matrix strongly influences gas transport, specifically in mixed gas permeation
  - Improvement of fiber performance for H_2/CO_2 separation with filler addition at 150 ºC is compromised at high operating feed pressures (30 bar)
- PBI/PVP blend asymmetric hollow fiber membranes
  - PVP addition: as spun fiber elasticity increases, industrially relevant take up rate values (25-50 m/min)
  - Mechanically robust and small diameter (< 300 µm) fibers have been successfully prepared
  - Blend fibers are thermally stable up to ~340 °C

Acknowledgement

This research has received funding from the European Union's Seventh Framework Programme (FP/2007-2013) under grant agreement number 608490 and Horizon 2020 research and innovation programme (H2020) under grant agreement n° 760944.

Thank you very much for your attention!

Questions

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Session 1B (chairperson Camel Makhloufi)	
11:15-11:35	Dr. M. Noponen and Dr. X. Sun - High temperature electrolysis and co-electrolysis
11:35-11:55	Prof. J Serra - Direct electrocatalytic conversion of CO_2 into chemical energy carriers in a co-ionic membrane reactor
11:55-12:15	Dr. V. Middelkoop - CO2Fokus at a glance: CO_2 utilisation focused on DME production, via 3D printed reactor and solid oxide cell based technologies
12:15-12:35	Dr. M. Tsampas - The KEROGREEN CO_2 plasma route to CO and alternative fuels
12:35-12:55	Dr. G. Bonura - 3D-printing in catalysis: Development of efficient hybrid systems for the direct hydrogenation of CO_2 to DME

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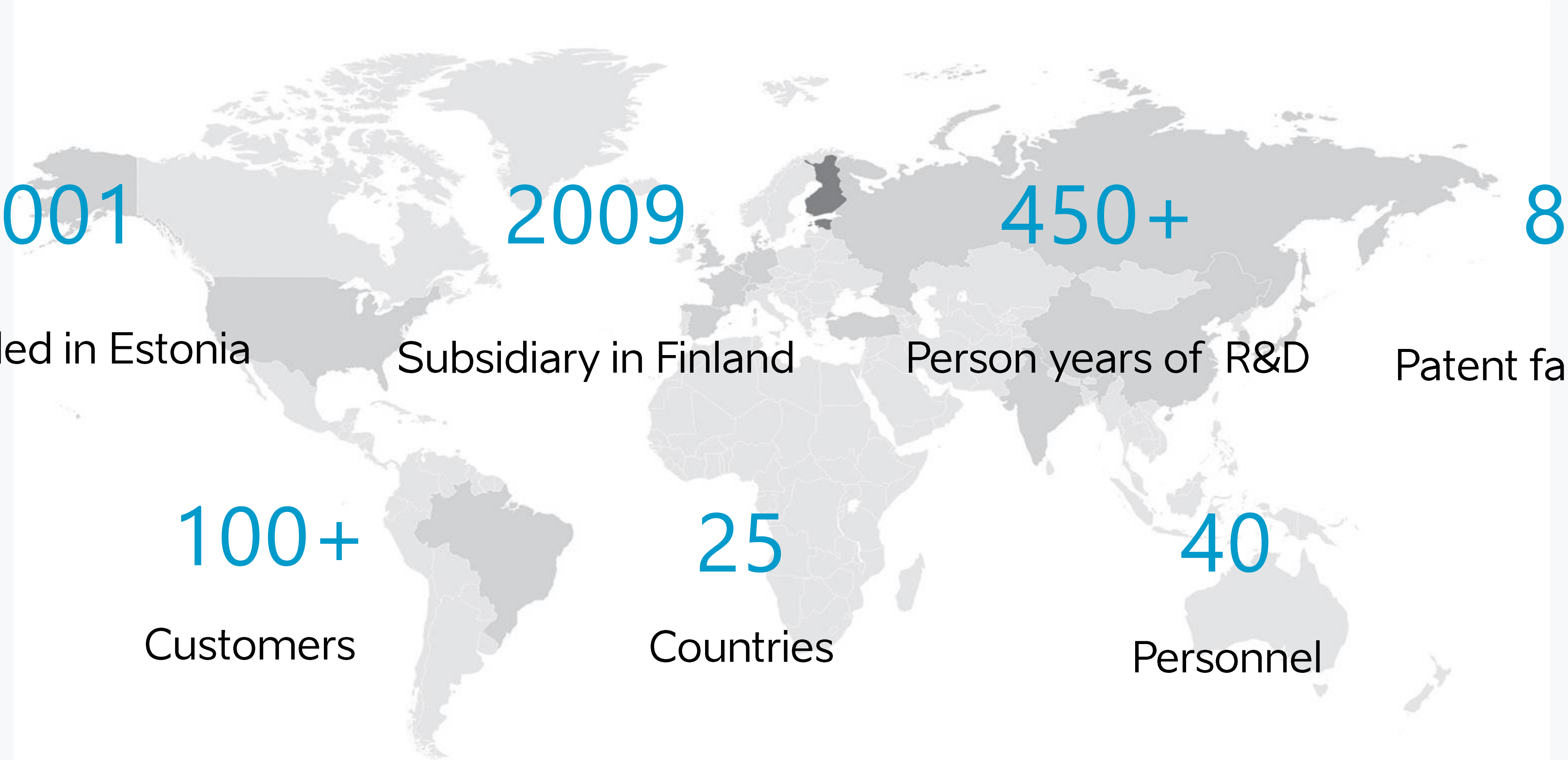
HIGH TEMPERATURE ELECTROLYSIS AND CO-ELECTROLYSIS

Matti Noponen, Timo Lehtinen (Elcogen)
Xiufu Sun (DTU)

PRESENTATION AGENDA

- Who We Are
- The Elcogen advantages
- C2FUEL project
- Acknowledgements

ELCOGEN AT A GLANCE



2001

Founded in Estonia

2009

Subsidiary in Finland

450+

Person years of R&D

8

Patent families

100+

Customers

25

Countries

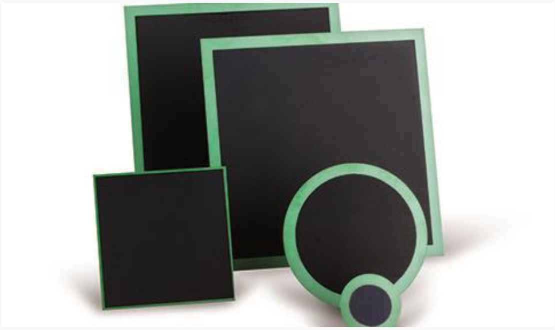
40

Personnel

Fuel cell technology
elcogen

ELCOGEN PRODUCT FAMILIES

- World-leading planar, ceramic, anode-supported cells (ASC). Patent-protected
- Low operating temperature of 650°C enables longer lifetimes
- Cells and stacks made with low cost raw materials and designed for mass manufacturing
- Low cost and uniquely designed SOCs drive major cost reductions at the system level



elcoCell

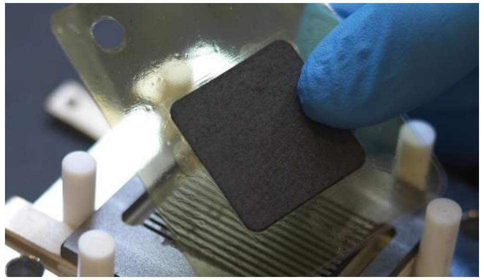
elcoStack

Fuel cell technology
elcogen

Department of Energy Conversion and Storage – DTU ENERGY

- Sustainable technologies for energy conversion and storage
- 230 researchers, technicians and PhD students
- Research spanning from fundamental investigations to component and prototype manufacture
- Focus on industrial collaboration and industrially relevant processes

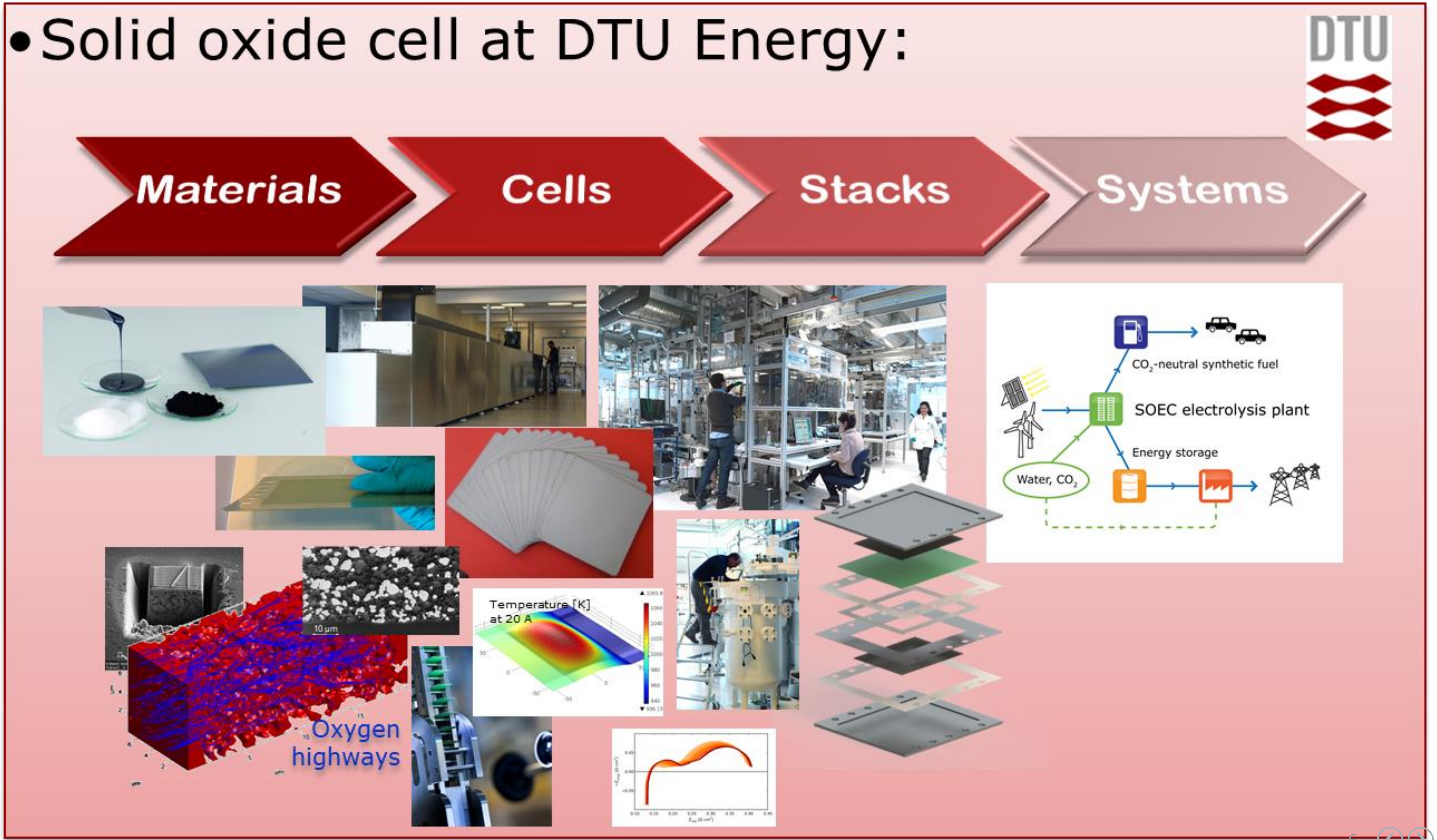

Solid oxide cells


Polymer exchange membrane cells


Batteries


Gas separation


Solar cells



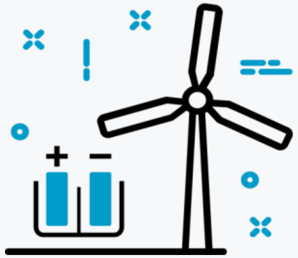
• Solid oxide cell at DTU Energy:
DTU
Materials
Cells
Stacks
Systems
CO2-neutral synthetic fuel
SOEC electrolysis plant
Energy storage
Water, CO2
10 µm
Temperature [K]
at 20 A
Oxygen
highways
6

SINGLE TECHNOLOGY – MULTIPLE APPLICATIONS

Residential: Single & Multi-Family

Commercial & Industrial CHP

Long-range Transportation



Electrolysers for Energy Storage and Power to Fuel

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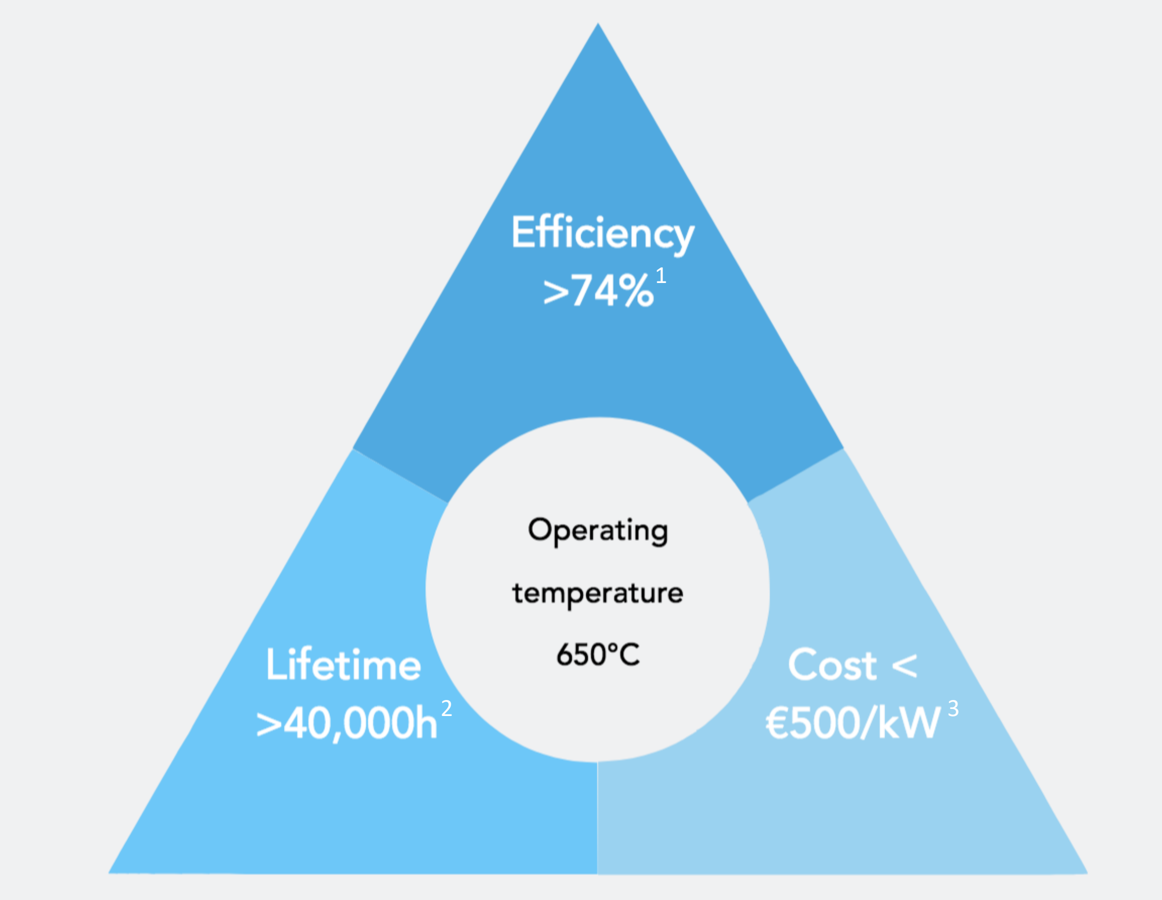
THE ELCOGEN ADVANTAGE



Elcogen is the SOC technology best positioned to address the 3 critical market barriers of Efficiency, Lifetime and Cost

Note: The targets in this chart apply to Elcogen stacks.

Note: [1]Elcogen's leading stack electrical efficiency of 74% (in fuel cell mode) has been measured with a 119-cell, commercial-grade 3kW stack using natural gas. [2]Durability of stack design has been proven through long-term tests reaching 20,000 hours, indicating a total lifetime of 40,000 hours for the stack. [3]Assumes a 1GW/year production capacity.

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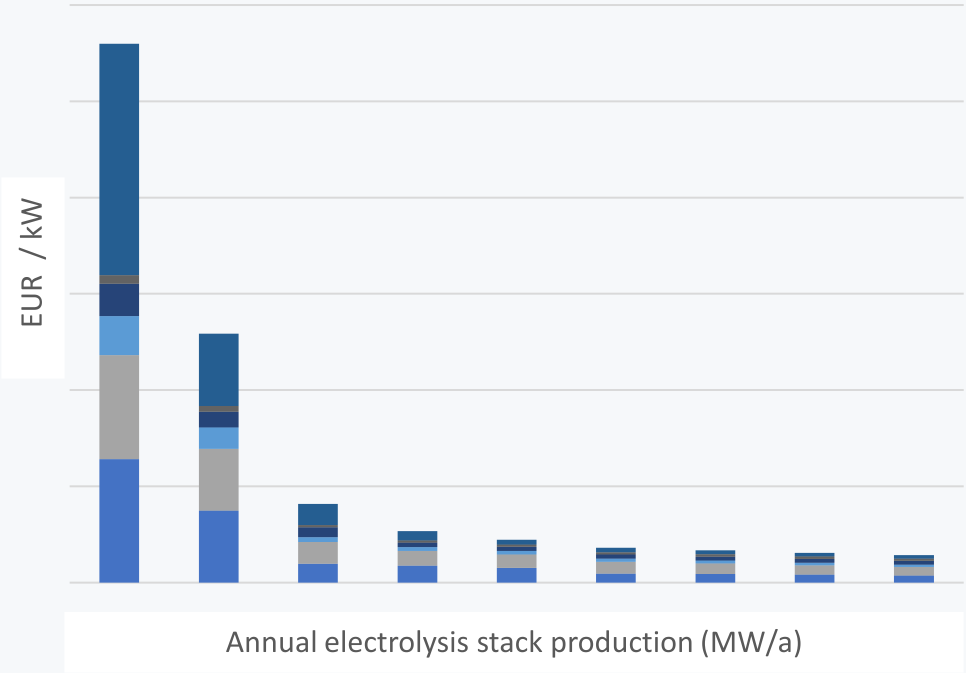
elcogen

ELCOGEN ADVANTAGE – COST

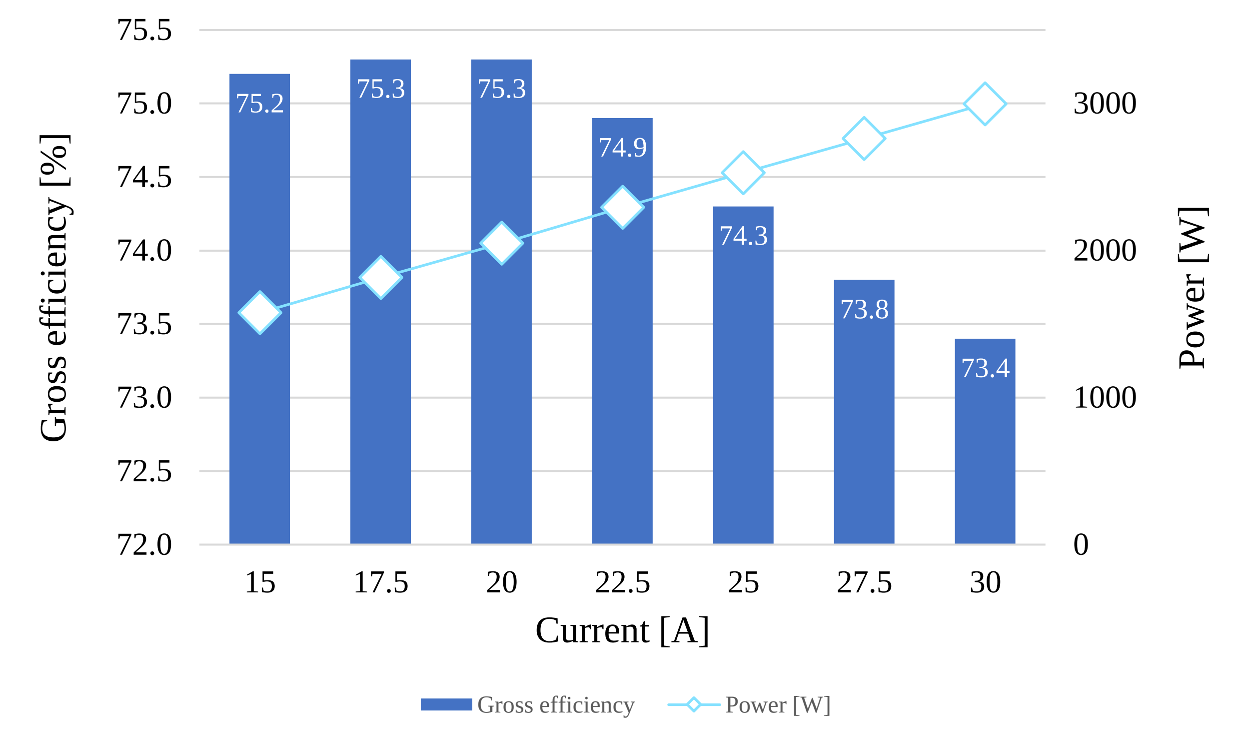
- Elcogen's stack cost analysed closely with the manufacturing partners
- Production volume is the main driver in cost reduction
- Elcogen has started a factory project with the aim to introduce 50 MW/a production capacity



Fuel cell technology
elcogen

THE ELCOGEN ADVANTAGE – EFFICIENCY (FUEL CELL)

- Ultra high energy conversion efficiencies are achieved with commercial E3000 stacks
- Elcogen stacks exceed 75 % efficiencies already at 600 °C (LHV, NG)
- The efficiency is enabled by unique, patent protected unit cell and stack designs



TEST CONDITIONS

Stack inlet temperature	590 °C
Fuel	Natural gas
Anode off gas recycle (sim.)	70 %
Air flow	330 Nl/min

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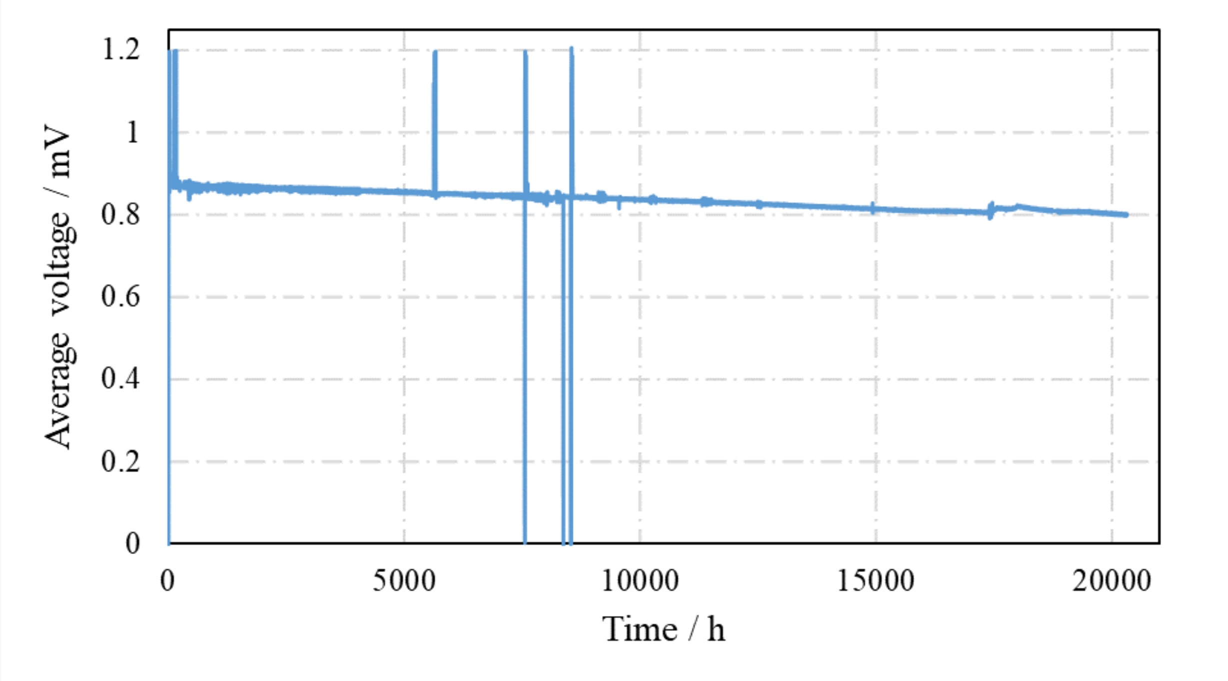
THE ELCOGEN ADVANTAGE – LIFETIME (FUEL CELL)

- Stack lifetime testing conducted in a real fuel cell systems
- Ongoing tests exceeding 20 000 hours
- Degradation rate linear with constant slope of 15 mΩ.cm^2 / 1000 h (i.e. 0.4 % / 1000 h)
- By assuming linear degradation, Elcogen stack technology has 40 000 hours lifetime expectation



TEST CONDITIONS

Stack inlet temperature	590 °C
Fuel	Natural gas
Fuel utilization	60 %
Steam-to-carbon ratio	2.2
Oxygen utilization	20 %

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A EUROPEAN RESEARCH & INNOVATION PROJECT

- This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 838014
- The project started on July 1st 2019, and will last 4 years (until 2023)
- Elcogen role is to provide high temperature steam electrolysis technology for the project (cell, stack and system)
- DTU role is to conduct cell and stack characterization and stack modelling in the project

C2FUEL

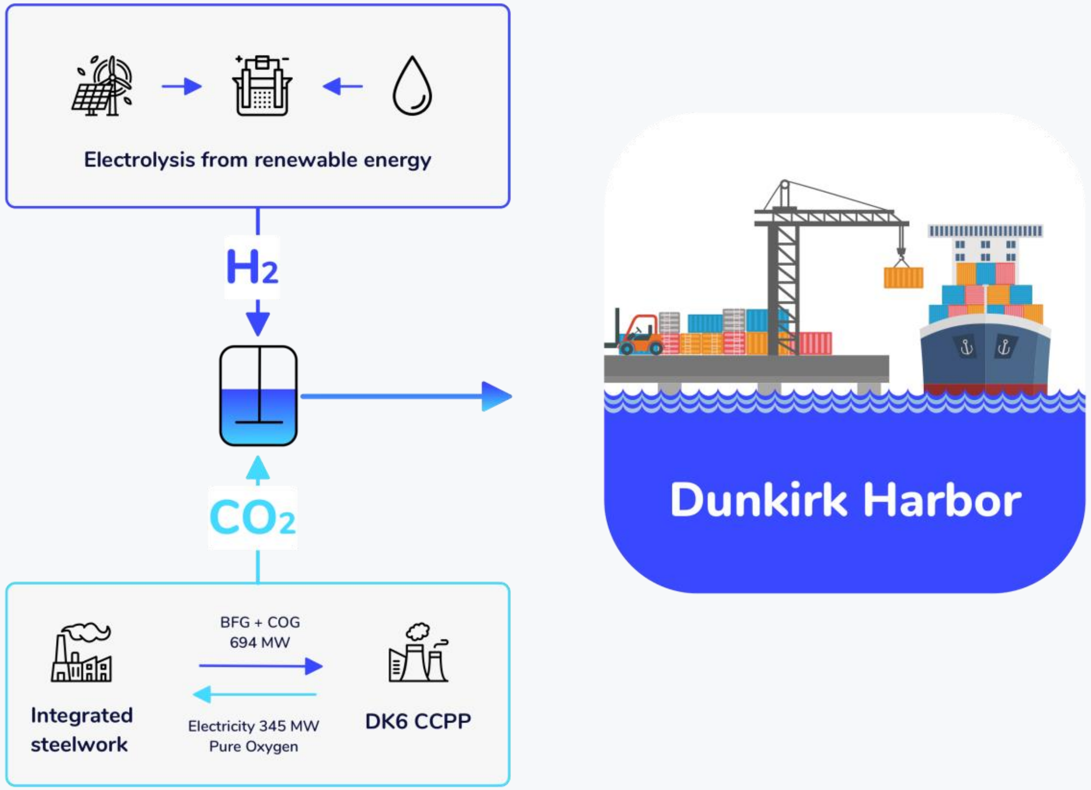
Fuel cell technology elcogen

DTU

C2FUEL OVERALL TARGET: 2.4 MILLION TCO2 AVOIDED PER YEAR

C2FUEL Project

Overall target 2.4 million tCO_2 avoided per year



Formic acid as Hydrogen carrier

Decreasing the electricity footprint during boat charging on docks

C2FUEL Output

2,4 million ton of FA

100 000 ton of green hydrogen

1,8 TWh of green electricity

Seasonal storage using 3.6 TWh of renewable electricity

Dimethylether as Maritime and truck fuel

Displacing fossil fuel emission from power plant and decreasing harbor mobility footprint

C2FUEL Output

1,2 million ton of DME

320 000 ton of green H_2 produced using 11 TWh of renewable electricity

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FROM TRL 3 TO TRL 6 ON INNOVATIVE TECHNOLOGIES

- C2FUEL partnership covers the whole value chain of conversion of CO2 for carbon-captured fuel production.

H_2 Generation

SOEC

Higher η

DTU Denmark Technical University

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CO_2 capture

Membrane contactor

Intensification

cnrs

ENGIE

DME production and use

Membrane reactor

DME Engine

Thermodyn.

Pollutant Emission

TU/e Technische Universiteit Eindhoven University of Technology

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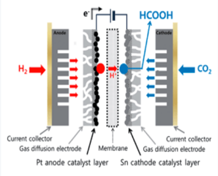
btd

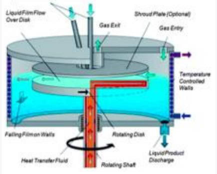
VOLKSWAGEN AKTIENGESELLSCHAFT

Formic acid production

Direct FA Coelectrolyzer



Spinning disc reactor



One step process

Intensification

TU/e Technische Universiteit Eindhoven University of Technology

ENGIE

FA reforming

Reformer and FC

Pressurized H_2

DENS DUTCH ENERGY SOLUTIONS

ENGIE

Demonstration

Integration and operation

Industrial environment

ENGIE

ENGIE ENGIE THERMIQUE FRANCE Centrale DK6

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STEAM ELECTROLYSIS VS CO-ELECTROLYSIS

EFFICIENCY IMPROVEMENTS THROUGH HT ELECTROLYSIS

$H_2O + 2e^- \rightarrow H_2 + O^=$

Reforming or other means

CO_2 capture

Synthesis gas

Liquid fuel synthesis

SIMPLIFIED PROCESS THROUGH CO-ELECTROLYSIS

$H_2O + 2e^- \rightarrow H_2 + O^=$

$CO_2 + 2e^- \rightarrow CO + O^=$

Synthesis gas

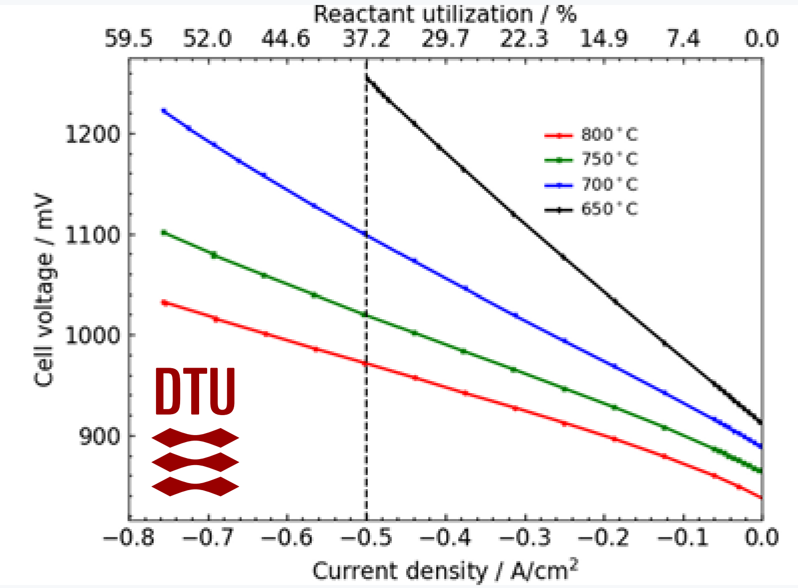
Liquid fuel synthesis

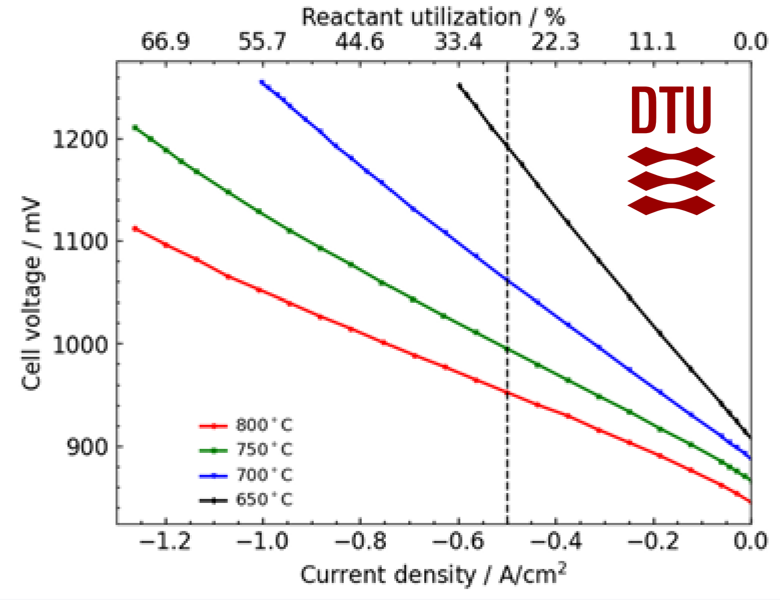
Fuel cell technology

elcogen

DTU

DETAILED CHARACTERIZATION OF UNIT CELLS





Steam electrolysis mode

Cathode flow rate	13.4 l/h
Inlet composition [H_2O, CO_2, H_2]	90 %, 0 %, 10 %

Co-electrolysis mode

Cathode flow rate	10 l/h
Inlet composition [H_2O, CO_2, H_2]	45 %, 45 %, 10 %

Specific energy consumption below 3.06 kWh/Nm^3 (1.28 V) at relevant current densities
Outlet composition in equilibrium determined by pressure, inlet gas composition, and temperature, current

Fuel cell technology
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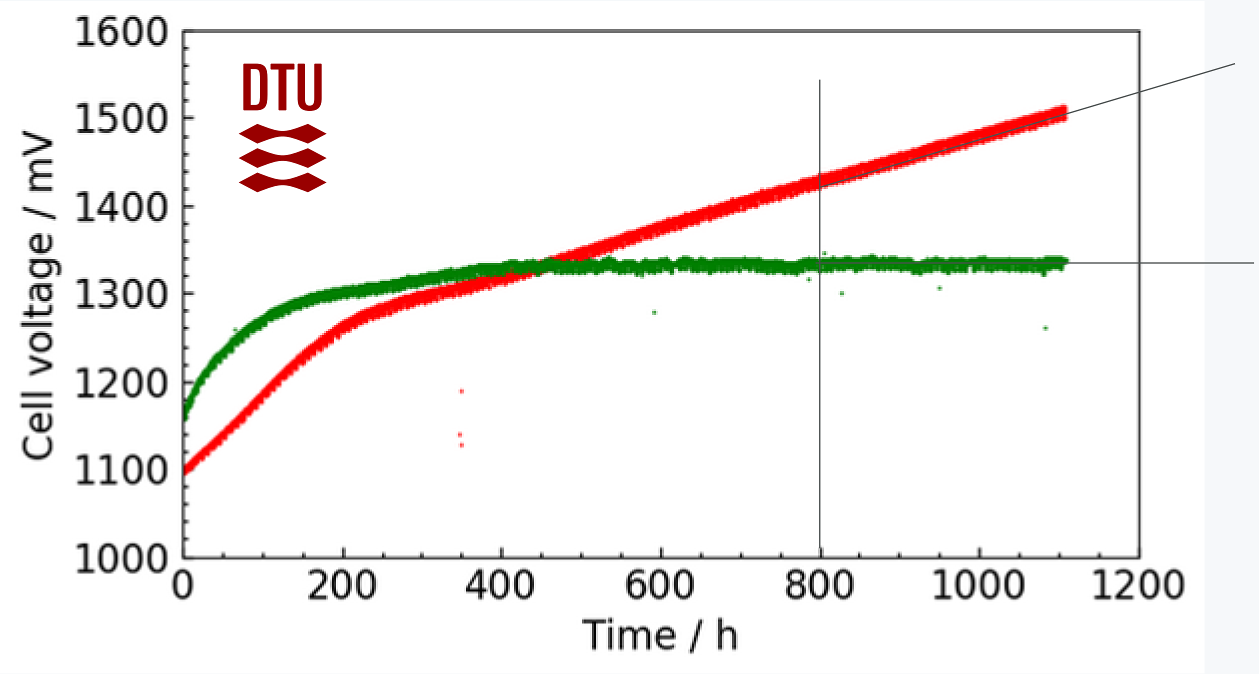
DEGRADATION TESTING AND LIFETIME LIMITING FACTORS

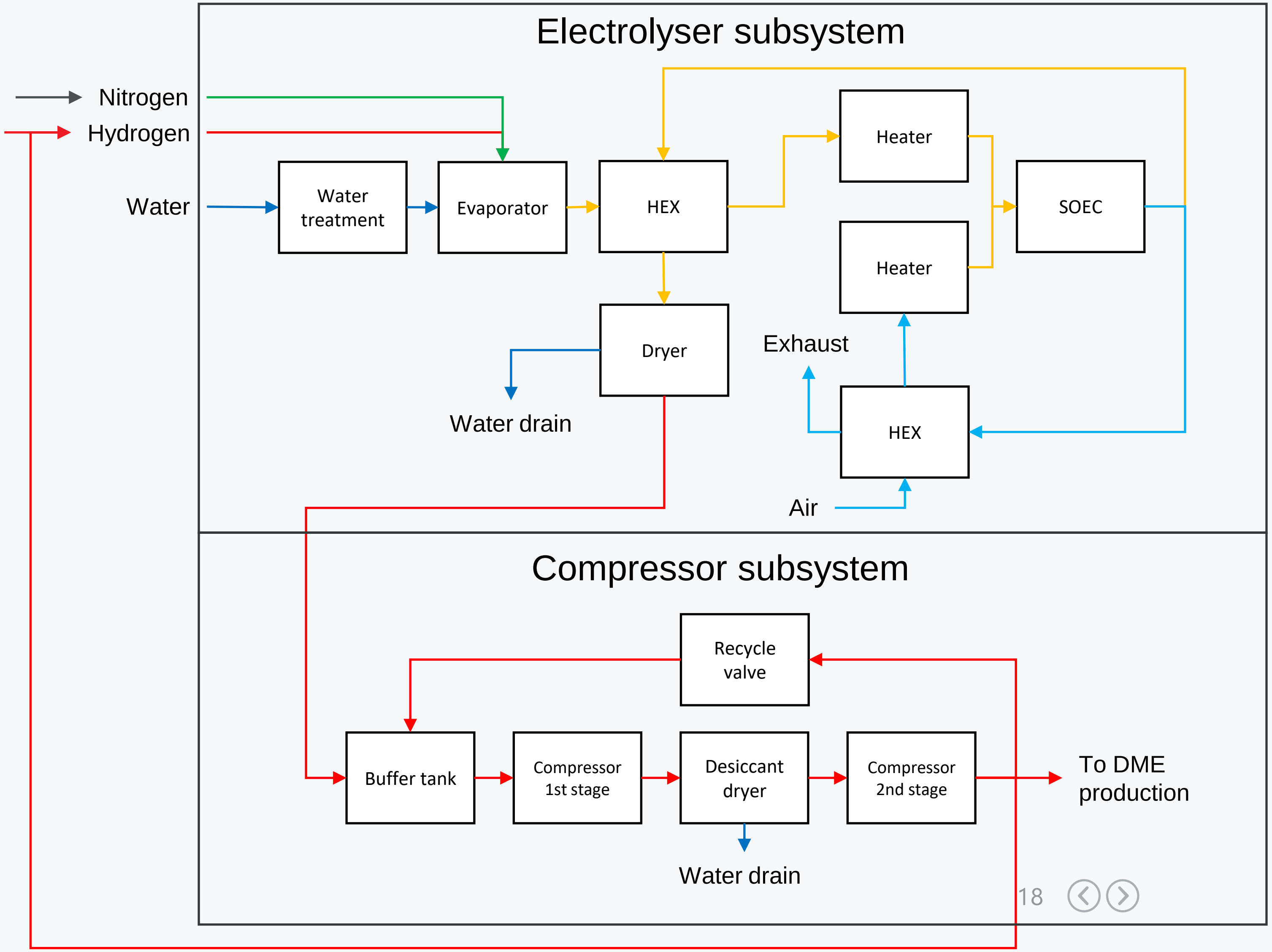
- Major focus on understanding lifetime limiting factors through long term experiments
- Example shows the importance for conducting the lifetime testing at different operation conditions
  - Test with different reactant utilizations
  - Degradation rate is changed from virtually zero (1 mOhm.cm²/kh) to rapid escalation (510 mOhm.cm²/kh)



Fuel cell technology
elcogen

SIMPLIFIED PI-DIAGRAM OF ELECTROLYSER DEMONSTRATOR

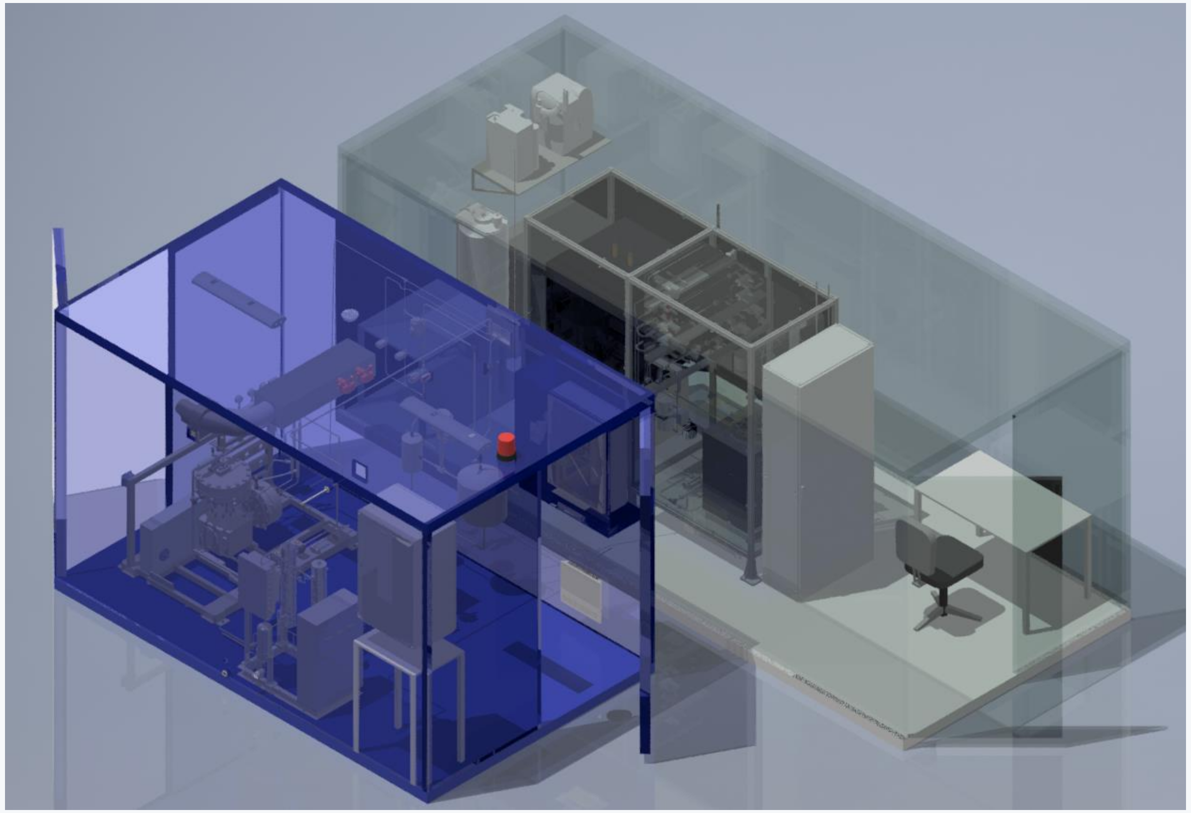
- SOE stack operation environment aimed to be designed as mild as possible
- Pressure level in stack as close to atmospheric as possible, pressurizing through diaphragm compressor
- Flow rates with large variation window
- Heat management via multiple mechanisms
- Hydrogen circulated back to stack inlet
- Water purification process highlighted in the process



Fuel cell technology elcogen

ELECTROLYSER DEMONSTRATOR

- The electrolyser unit and compression system are installed into containers
- Containers are designed modular and can be operated independently
- Electrolysis system designed to produce 1Nm^3/h of atmospheric pressure hydrogen from Type I water
- Compressor container system compresses produced hydrogen to 40 bar and dries it to -60°C dew point (ref. atm. pressure) equals to ~19 ppmVOL
- Containers will be installed outdoors at the DK6 site with other bricks of the C2FUEL project demonstration system



Layouts of compressor (left) and electrolyser (right) containers

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ACKNOWLEDGEMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 838014.

THANK YOU FOR YOUR ATTENTION!

Fuel cell technology
elcogen

Direct electrocatalytic conversion of CO_2 into chemical energy carriers in a co-ionic membrane reactor

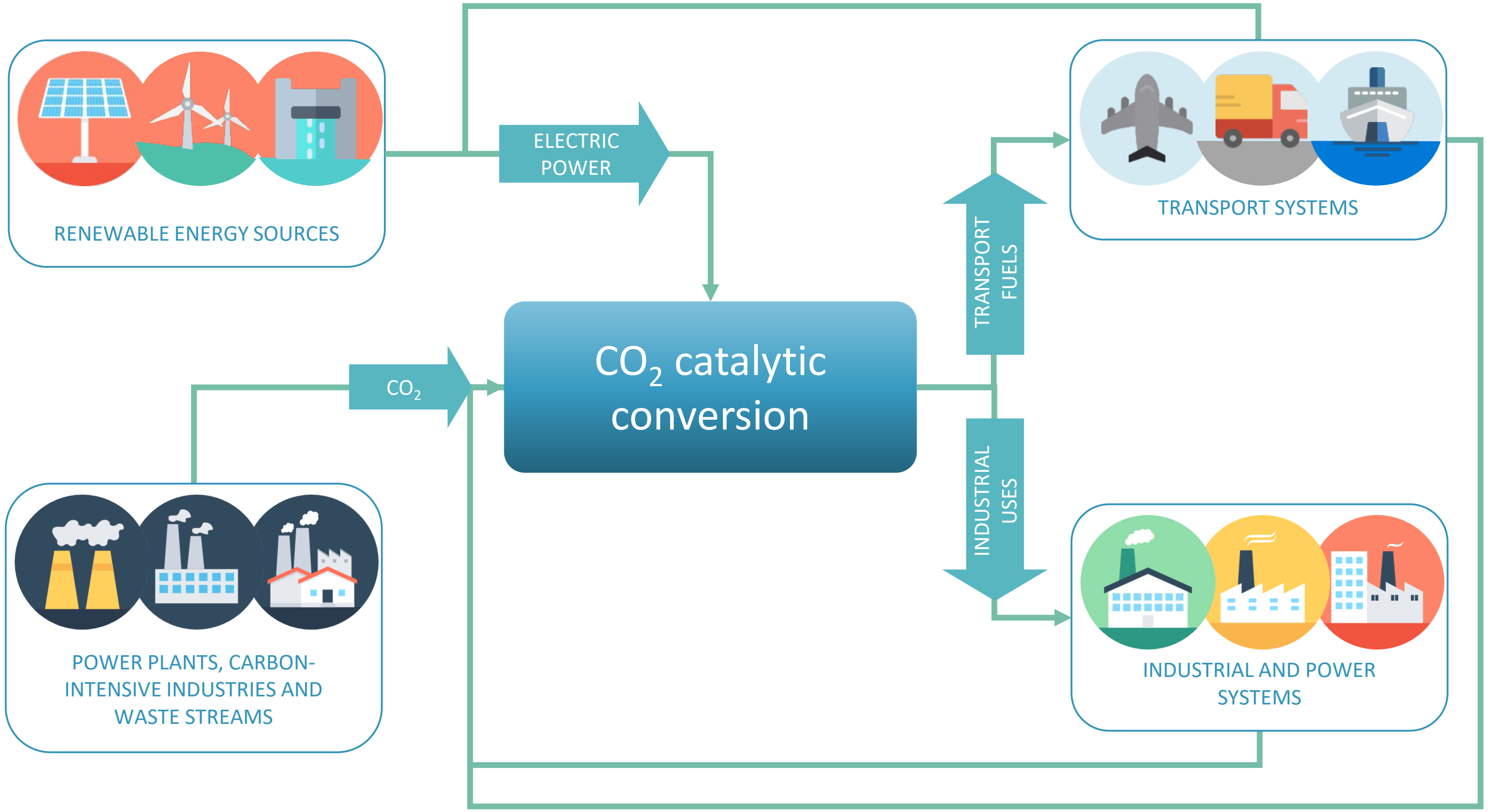
José M. Serra

This project has received European Union's Horizon 2020 research and innovation funding under grant agreement Nº 838077.

Context

CO_2 catalytic conversion

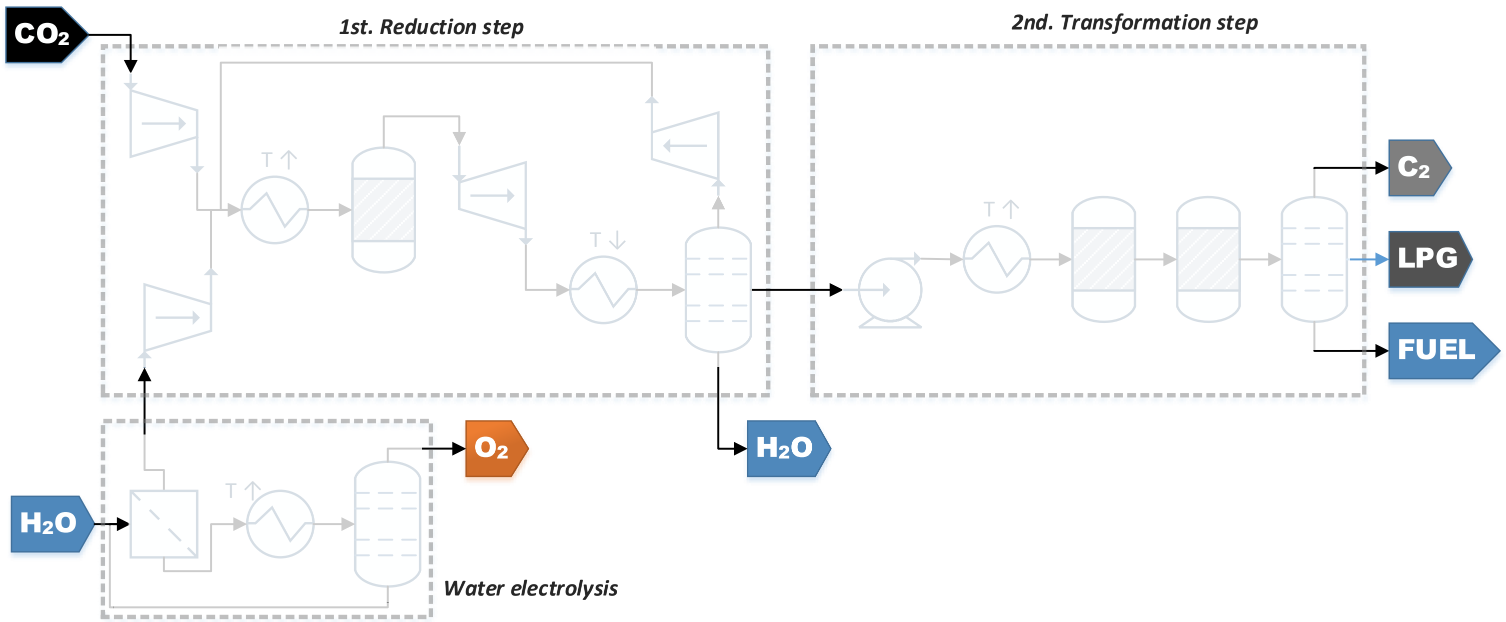
combined solution for energy storage and carbon footprint reduction



Sustainable Process Industry through Resource and Energy Efficiency

Context

Current CO_2-to-fuel technologies



Multi-step approach
involves a sequence of separated processes

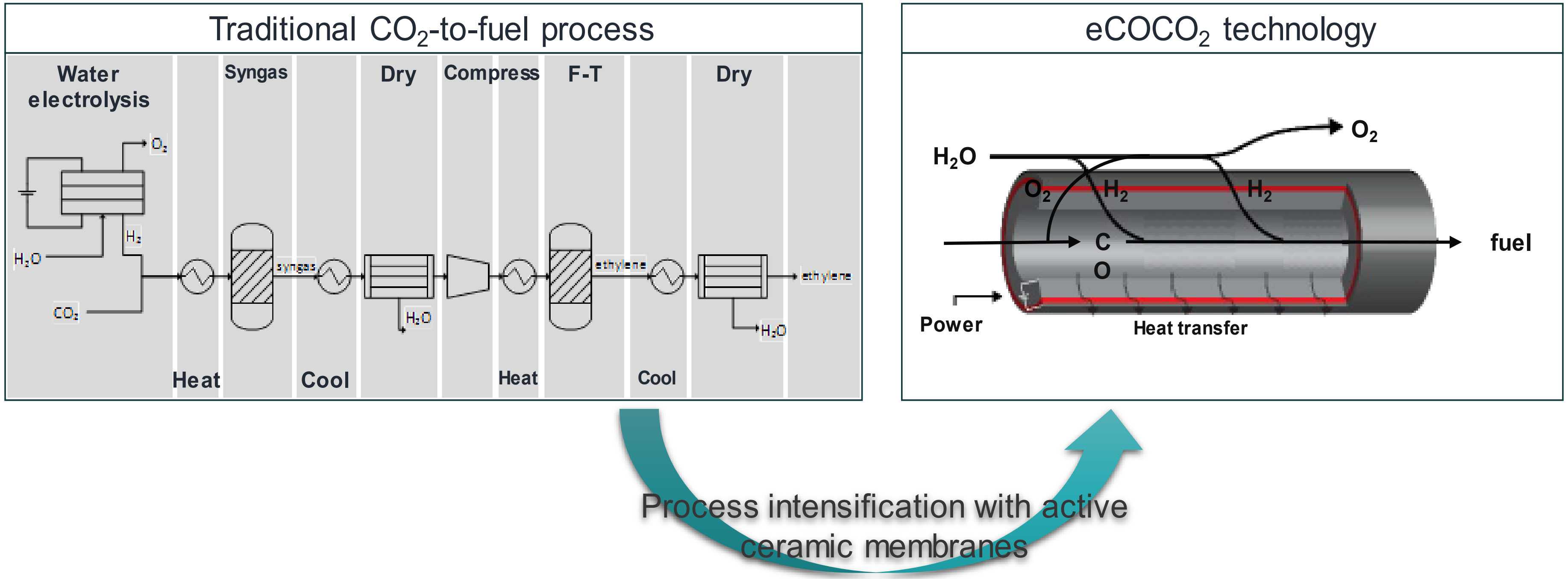
High costs
up to 300 €/ MWh CAPEX and 750 €/MWh OPEX

Highly energy intensive
with overall energy efficiency values around 60%

$eCOCO_2$ Approach

Single-step electrolysis and one-pot catalytic conversion

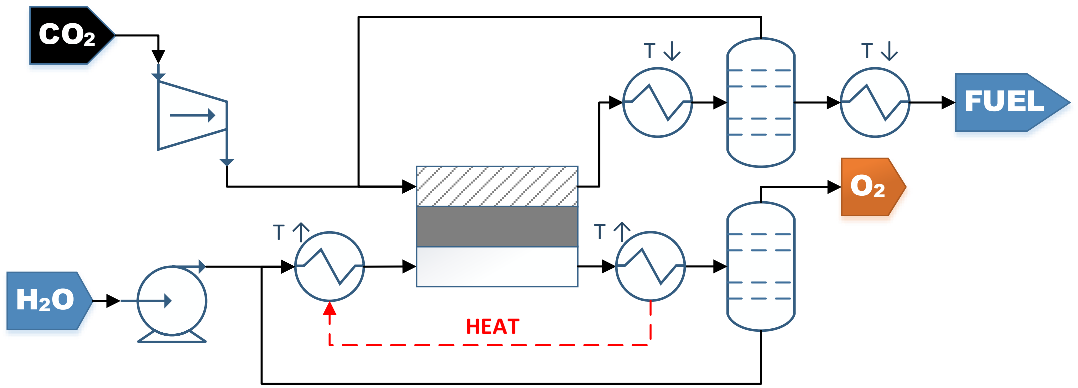
Membrane Reactor for the direct electrocatalytic conversion of CO_2 and steam into hydrocarbons



Scientific background and techno-economics: Malerød-Fjeld et al., **Nature Energy 2017**, Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss, https://www.nature.com/articles/s41560-017-0029-4

$eCOCO_2$ Approach

(Intensified) Single-step electrolysis and one-pot catalytic conversion



Product:
Jet fuel

Efficiency:
> 85%

Full integration:
compact sized reactor

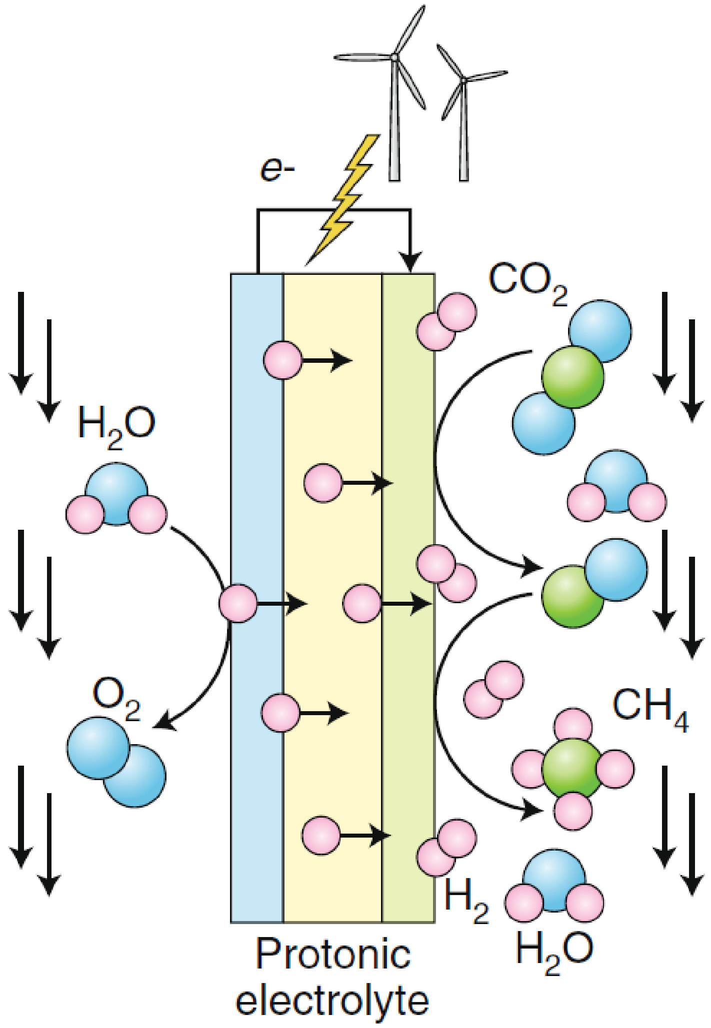
Final TRL:
5

Set-up a technology for conversion of CO_2, using renewable electricity and water steam, to carbon-neutral jet fuel, at high energy efficiency, very high CO_2 conversion rate and moderate-to-low cost.

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

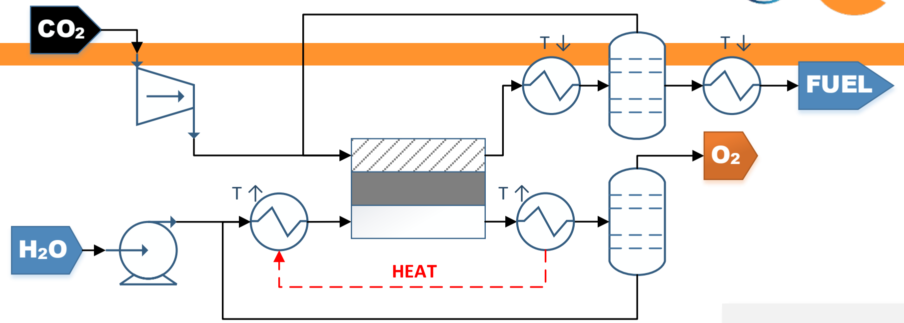
eCOCO$_2$ Approach

Single-step electrolysis and one-pot catalytic conversion



“Electrifying chemistry with protonic cells”, **Nature Energy** 4 (3) (**2019**) 178-179

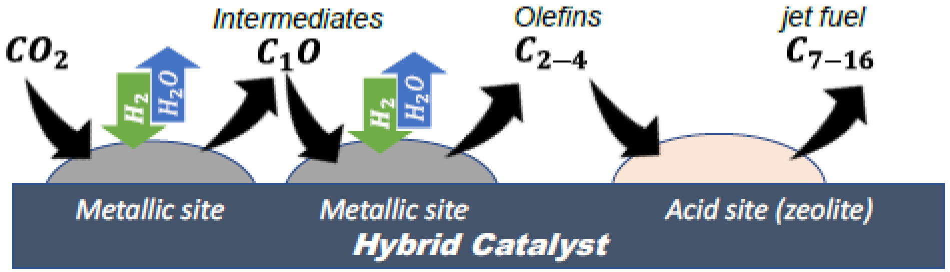
$eCOCO_2$ Approach



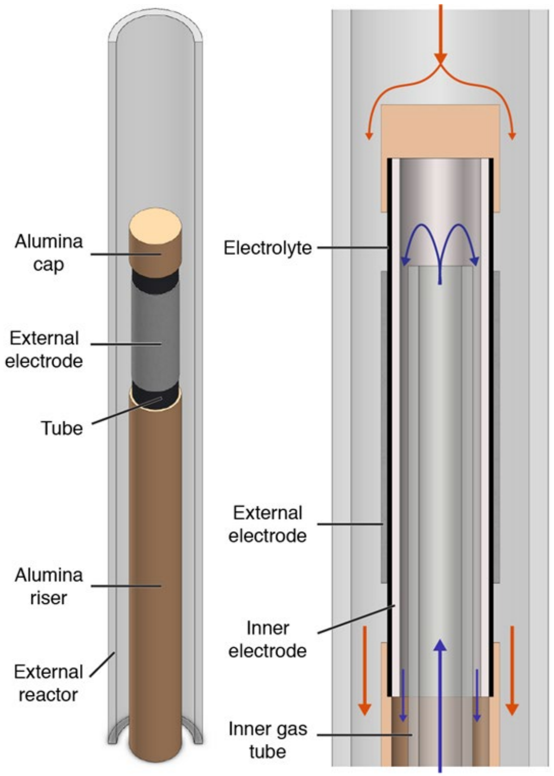
Concepts behind the intensification

Enabling Components

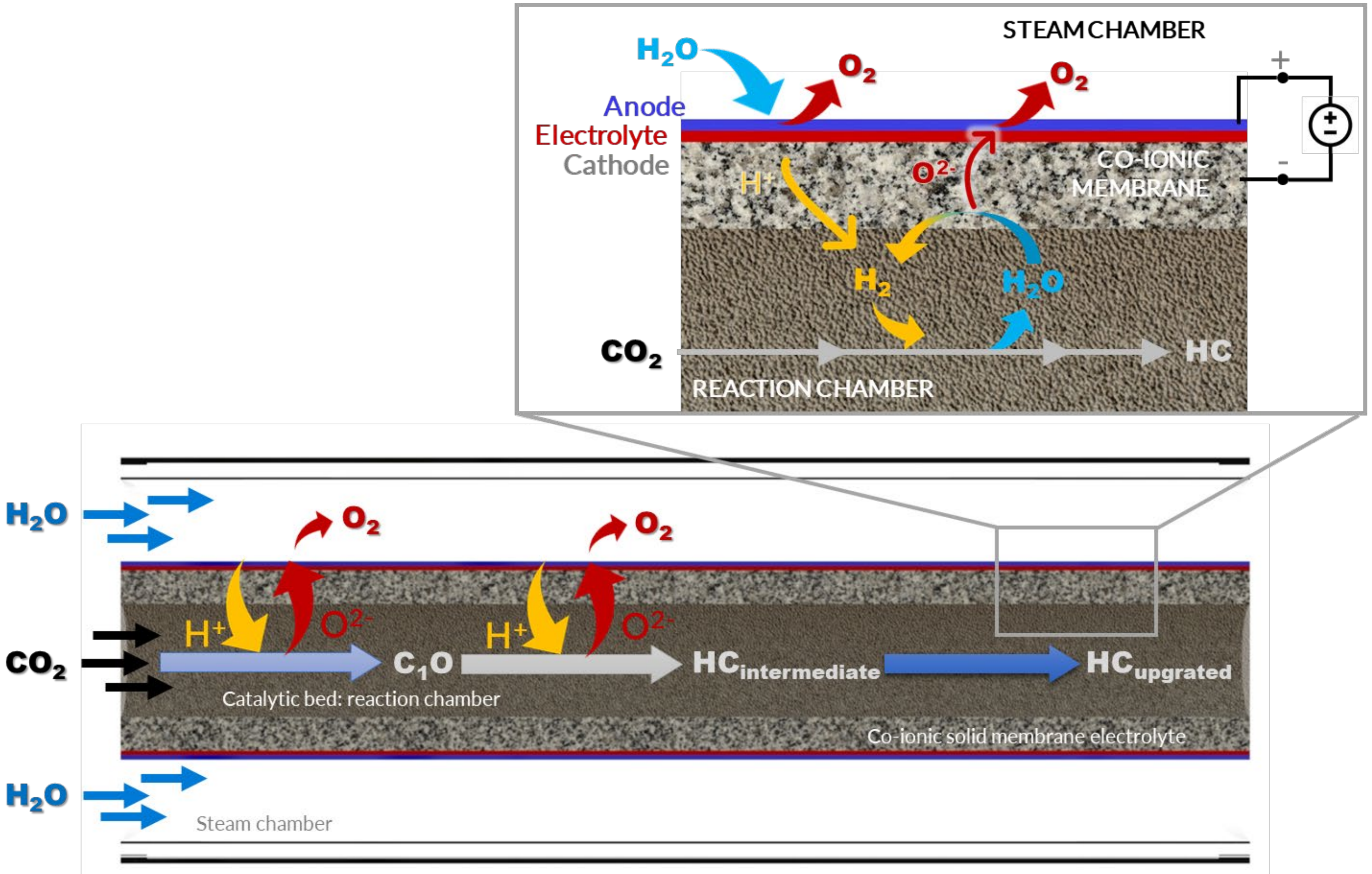
- In-situ **heat** integration: Integrating chemical **reactor** and water **electrolyzer** balance exothermic HC synthesis and endothermic water splitting — **Compact EC-reactor**
- Shifting the **equilibrium** by removing the H_2O formed in the CO_2 hydrogenation
- Avoid the effect of **high *p*H_2O** in kinetics and catalyst degradation (e.g. zeolite) at high X_{CO2} — **Co-ionic Electrolyte**
- Control of pH_2 along the reactor favors conversion to target products
- Sequential catalytic reactions: RWGS + Intermediate formation + target hydrocarbons — **Hybrid Catalyst**



$eCOCO_2$ Approach



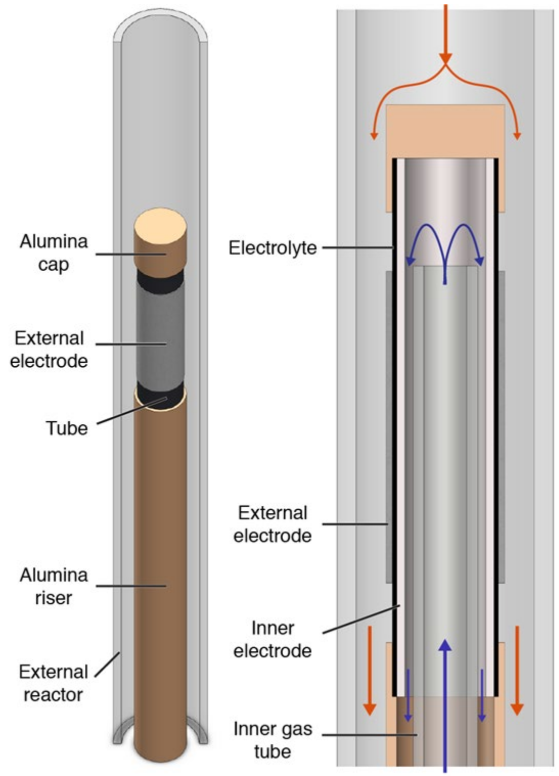
E. Vøllestad, et al. “Mixed Proton and Electron Conducting Double Perovskite Anodes for Stable and Efficient Tubular Proton Ceramic Electrolysers”, **Nature Materials 2019**

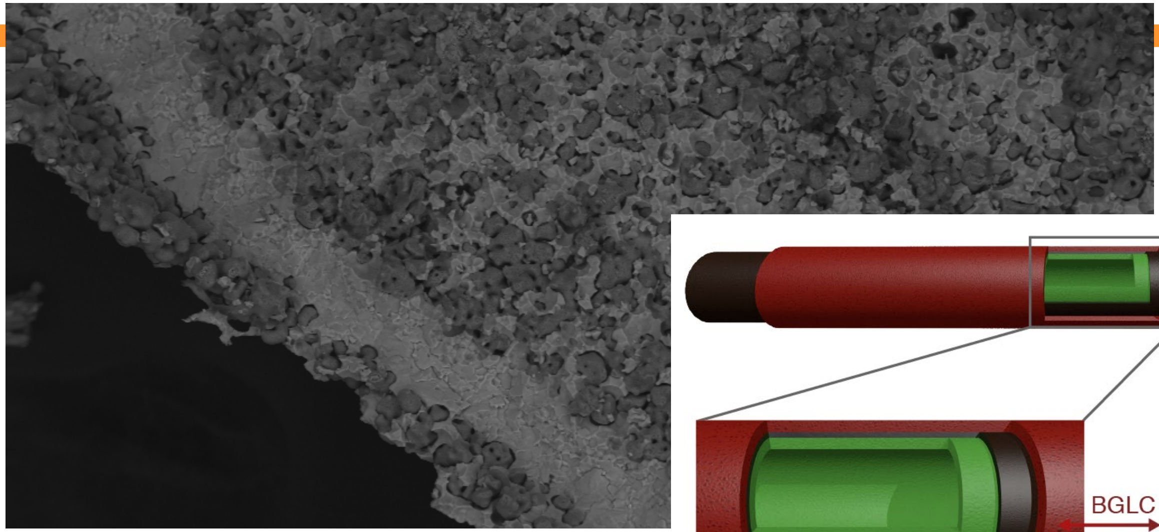


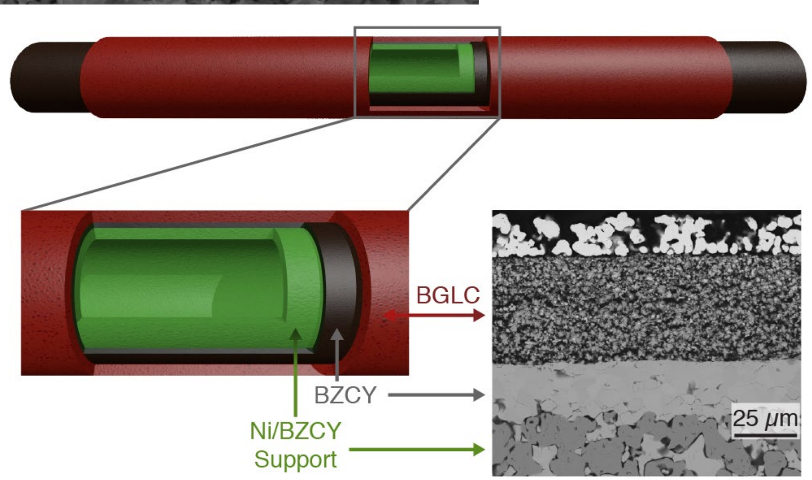
HC: hidrocarbons (intermediate: C2-C10; upgrated: C8-C16)

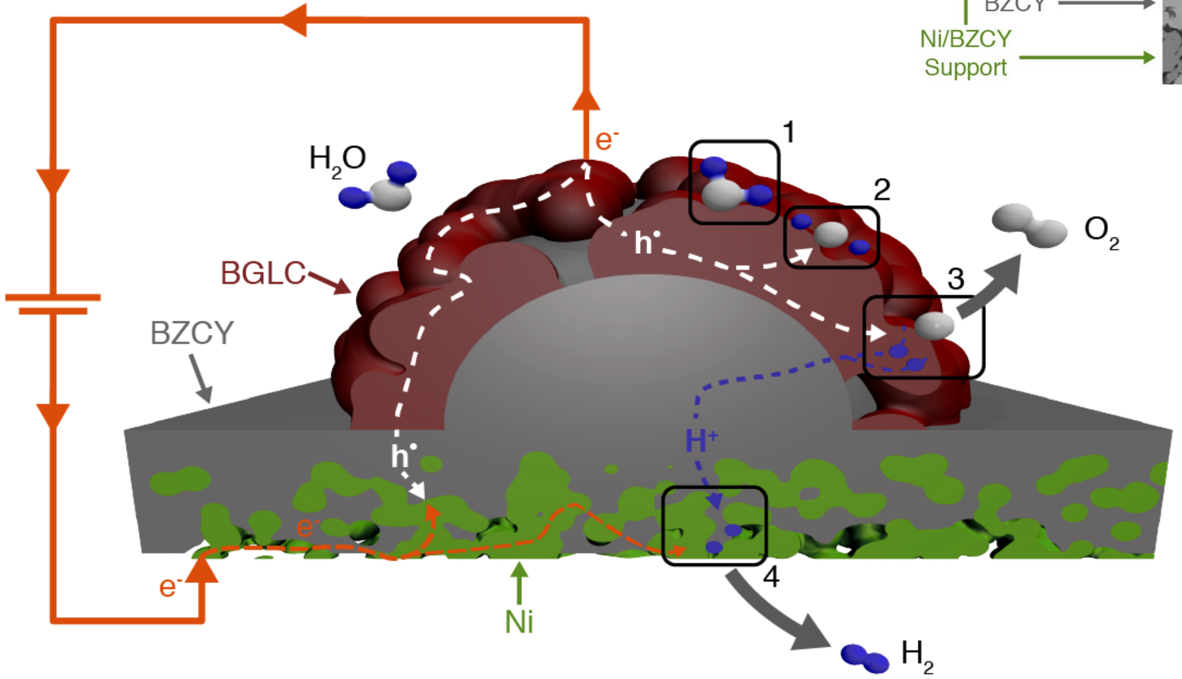
$eCOCO_2$ Approach

Reference cells



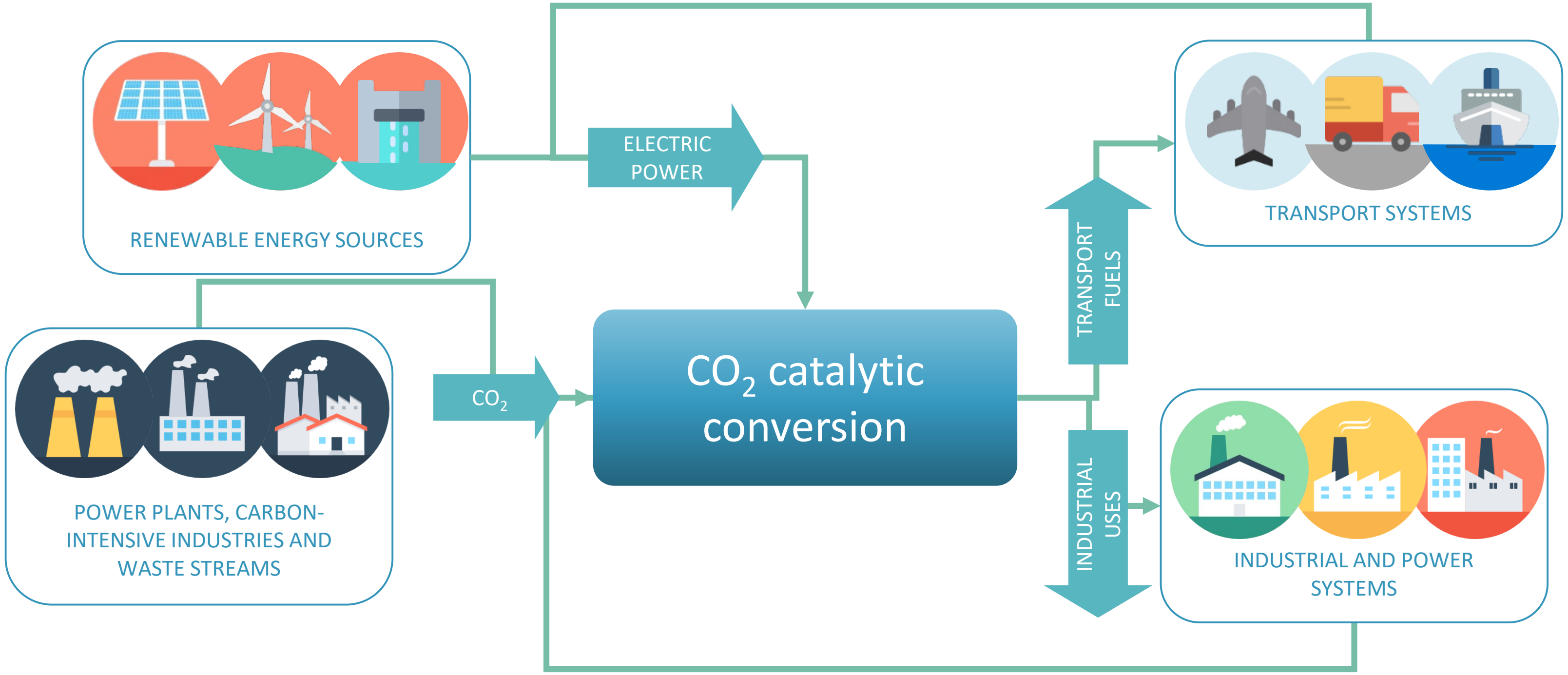






E. Vøllestad, et al. "Mixed Proton and Electron Conducting Double Perovskite Anodes for Stable and Efficient Tubular Proton Ceramic Electrolysers", **Nature Materials 2019**

Context



Challenges

- Couple Catalysis and Electrochemical Cell operation conditions
- Manufacture of large cells with novel components
- CO_2 streams: composition, conditions, capture&cleaning costs…
- Integration in industrial processes: TEA
- Social perception and acceptance

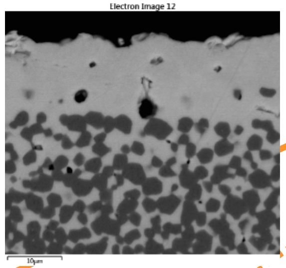
Objectives

1
Co-ionic electrolyte
Adequate H^+/O^{2-} conductivity

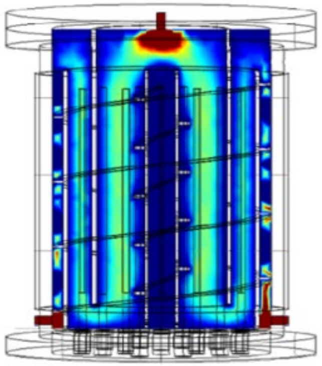
2
Electrodes
Active, selective and stable

3
Hybrid catalyst
In-situ reduction of CO_2 to jet fuel hydrocarbon fractions

4
Electrochemical cells
Manufacturing demonstration



Tubular reactors
Composed by electrochemical cells and structured catalyst



5
Multi-tube reactor
Stable and effective operation demonstration

6
Integrated process
Techno-economical and environmental validation

7
Societal perception
Assessment, model and prediction

Sustainable Process Industry through Resource and Energy Efficiency

Partners

eCOCO2

The consortium is formed by well balance of reference research and academic institutions:

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

UNIVERSITAS OSLOENSIS MDCCCXI

UNIVERSITAT POLITÈCNICA DE VALÈNCIA

RWTH AACHEN UNIVERSITY

SINTEF

九州大学
KYUSHU UNIVERSITY

UNIVERSITAS AMOIENSIS

and leader companies:

COORSTEK MEMBRANE SCIENCES

HERA

CEMEX

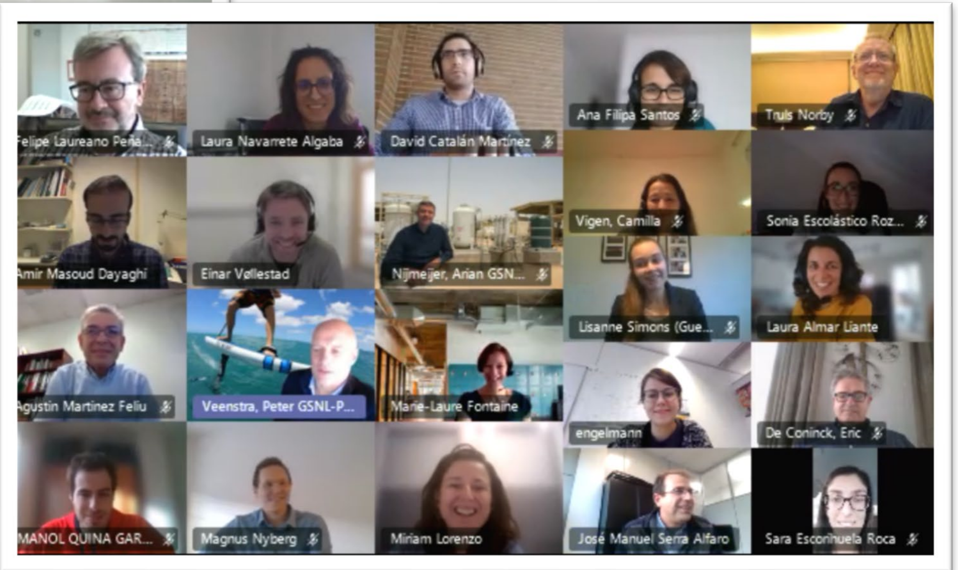
ArcelorMittal

Shell

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

Teams

Equal opportunities between men and women in the implementation of the action are promoted. Gender balance at all levels of personnel assigned to the action, including at supervisory and managerial level.



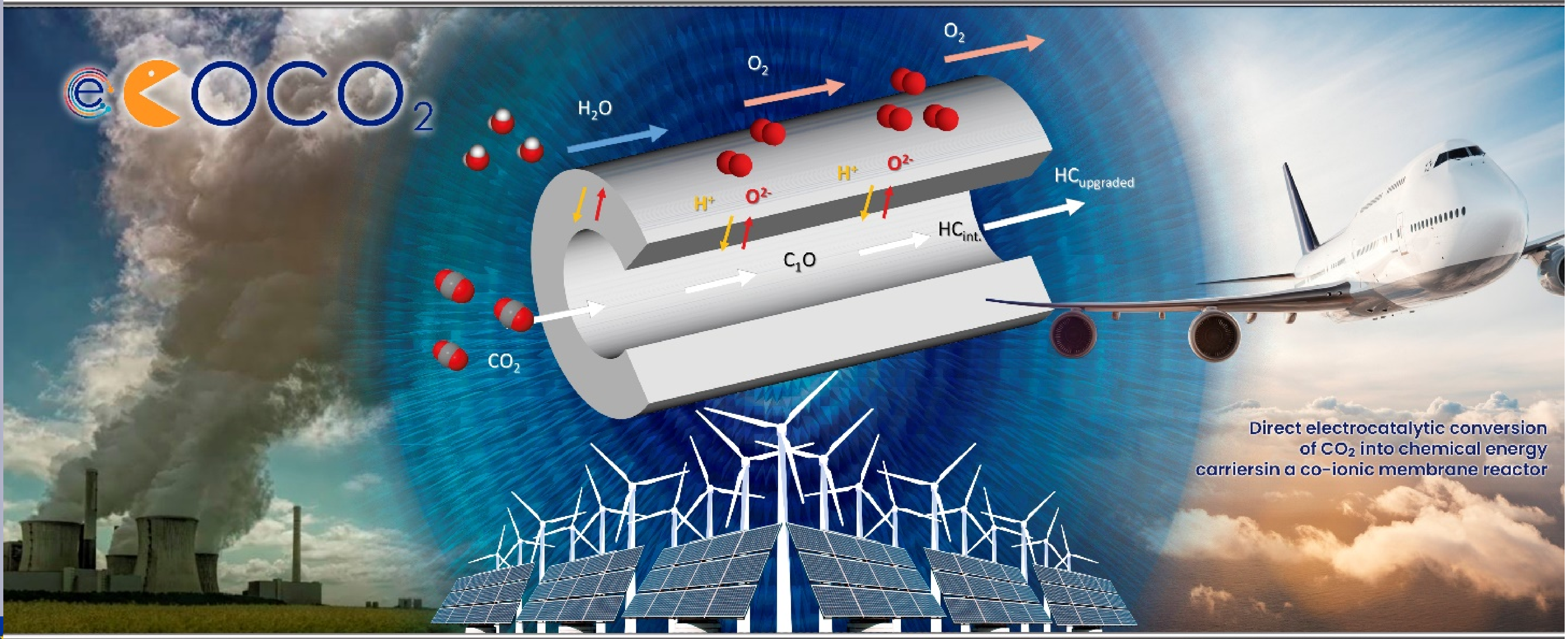
5 Women
WP Leaders

Barriers

- **Economic sustainability of the process**
  - Associated costs, including capital costs and operating costs (mainly energy consumption), and the expected savings and revenues.
- **Dependence on upstream technologies**
- **Availability of required associated infrastructure**
- **Public perception and acceptance of the technology**
- **Regulatory barriers**

Sustainable Process Industry through Resource and Energy Efficiency

Dissemination and Communication



- ✓ Website ecocoo.eu
- ✓ Social networks
- ✓ Visual identity
- ✓ Press release and radio
- ✓ Project flyer
- ✓ Project video

FOLLOW US!

SPIRE Sustainable Process Industry through Resource and Energy Efficiency https://ecocoo.eu

twitter.com/eCOCOO2/

linkedin.com/company/ecoco2/

YouTube channel: eCOCO2 H2020

This project has received European Union's Horizon 2020 research and innovation funding under grant agreement Nº 838077.

Sustainable Process Industry through Resource and Energy Efficiency

INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILISATION

CO_2FOKUS

ADVANCING CO_2 CONVERSION

CO_2 utilisation focused on market relevant dimethyl ether production, via 3D printed reactor and solid oxide cell based technologies

Vesna Middelkoop

16 February 2021

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The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

info@co2fokus.eu

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

CO_2Fokus facts and figures

12
PARTNERS

42
MONTHS

2019/07/01
STARTING DATE

8
COUNTRIES

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

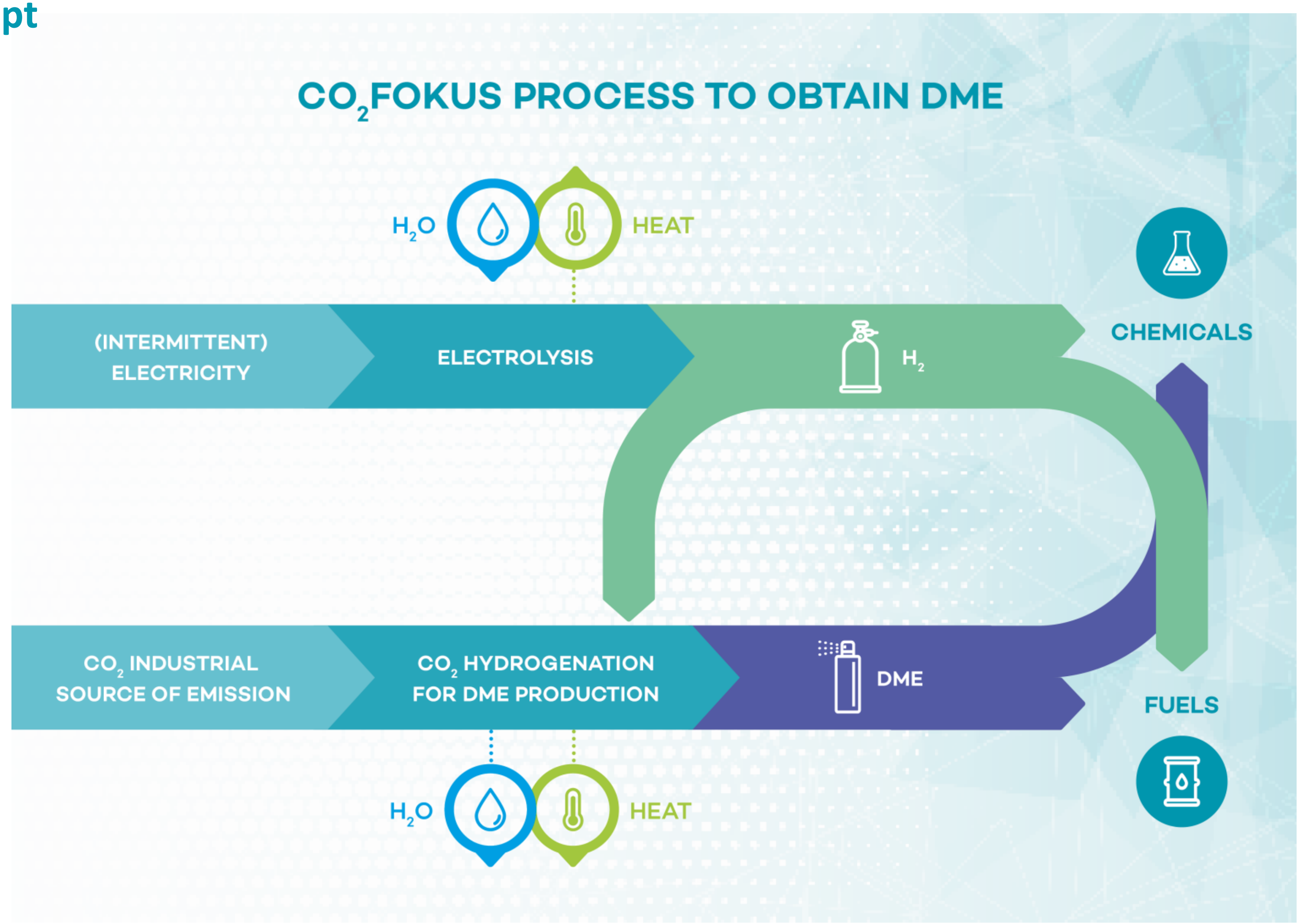
CO_2Fokus at a glance

The project will develop a cutting-edge technology to directly convert industrial CO2 into DME (Dimethyl Ether), by:

- employing innovative 3D printed multichannel catalytic reactors and solid oxide electrolyser cells
- integrating and testing them in an industrial environment of large industrial CO2 point sources

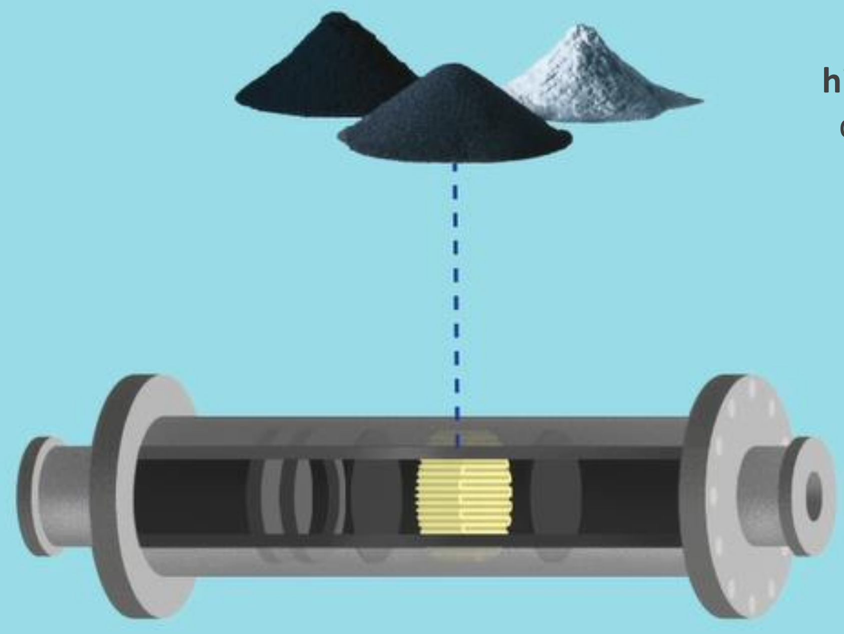
The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Concept



The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Catalyst formulation and single tube catalyst screening for DME production

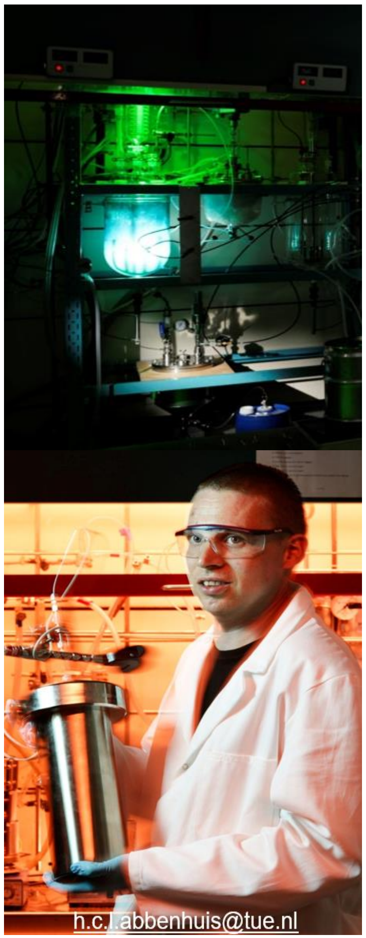


high selectivity and conversion for the direct hydrogenation of CO_2 to DME

multi-channel catalytic reactor with highly favourable heat and mass transfer properties and a low pressure drop

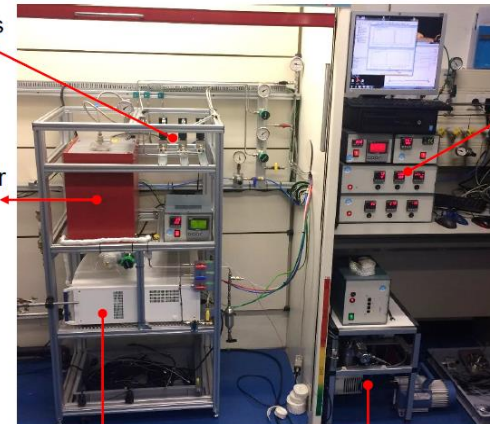
The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Catalyst formulation and single tube catalyst screening for DME production



MFC's for gas flow control

Reactor oven

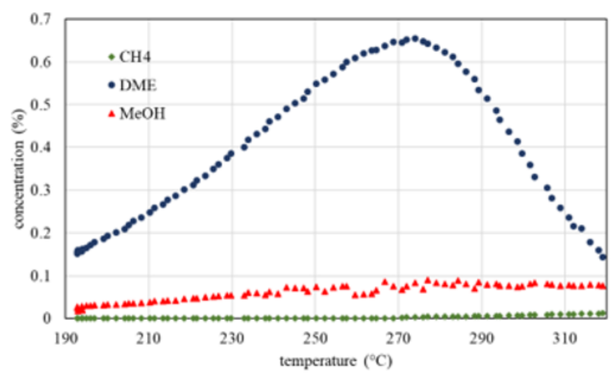


Gas and temperature control + online data logging of:

- Pressure
- Temperature
- Flows
- MS
- GC

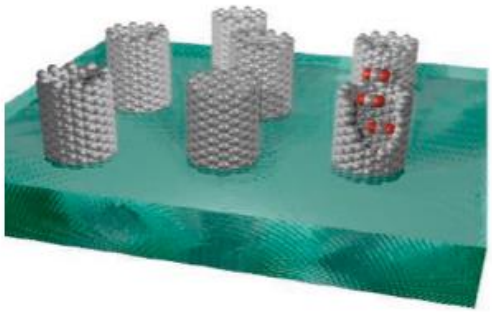
Compact GC with both FID and TCD channel

Mass spectrometer for inline analysis

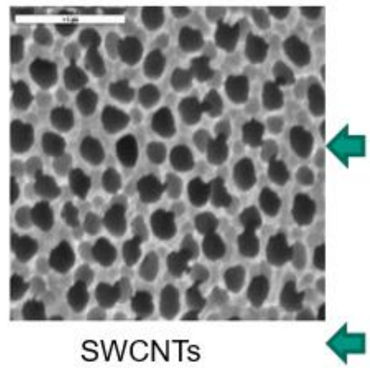


The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

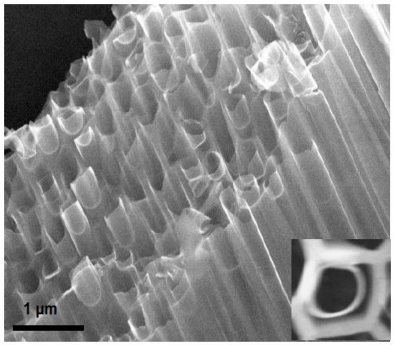
Single tube catalytic CNT membrane reactors for DME production



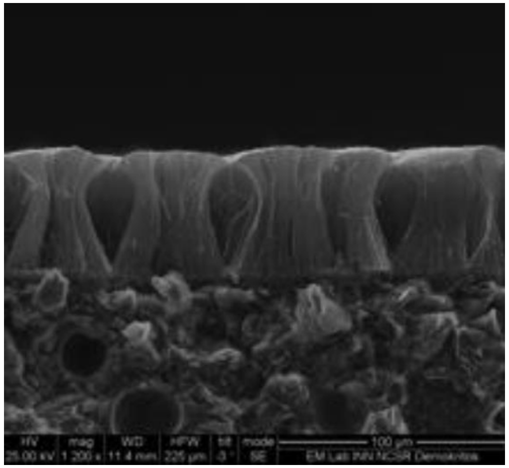
Aligned Carbon Nanotube (ACNT)s:

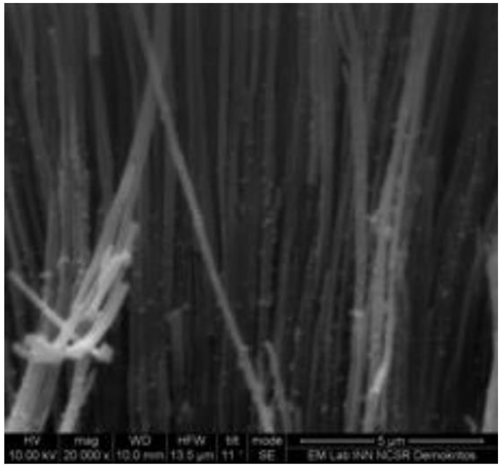


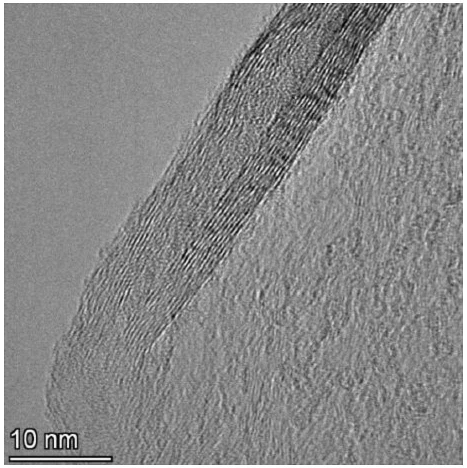
SWCNTs



parallel catalytic nanoreactors







Tailored nano pore size by Atomic Layer Deposition (ALD)

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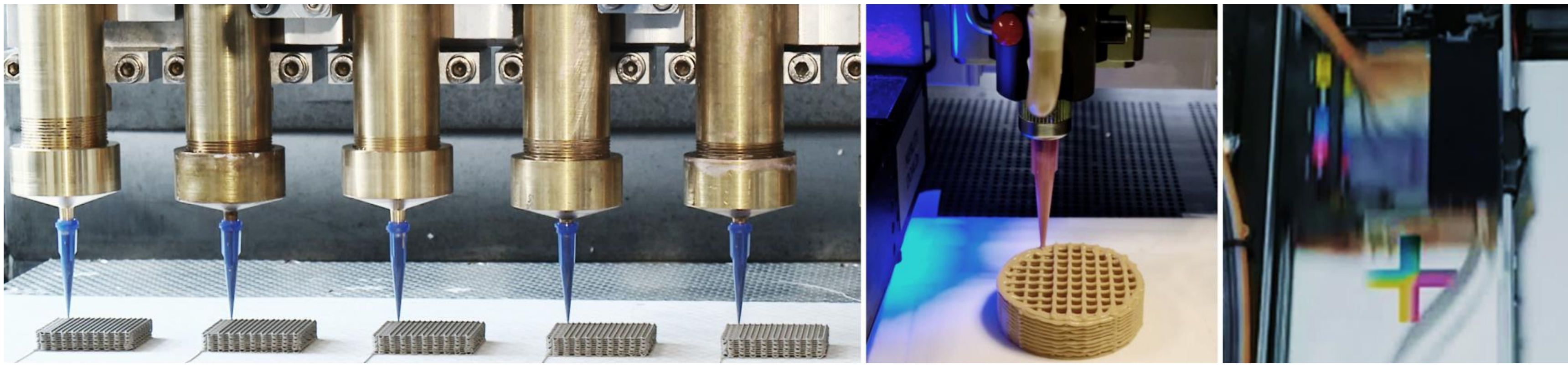
Why do 3D printing of catalysts and adsorbents?

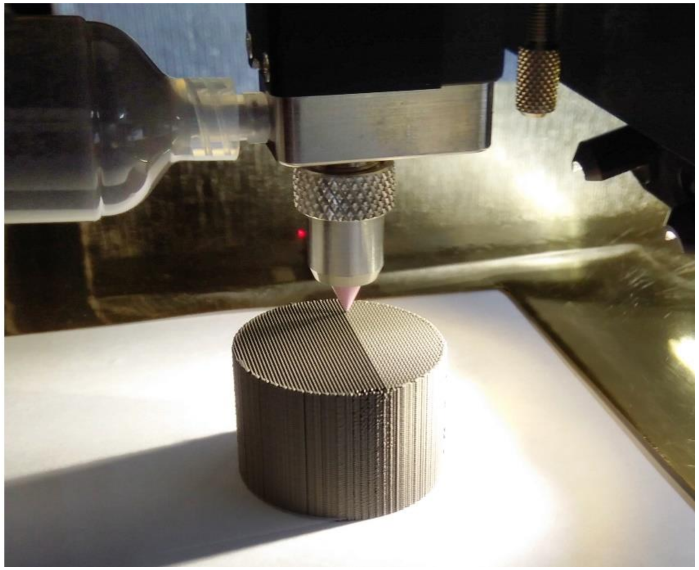


Major advantages of 'direct write' (structuring reactors into multi-channel, multi-layer architectures) is that tailor-made multi-modal devices allow for:

- **precise and uniform distribution of active material over a high surface area**
- **highly adaptable and well-controlled design for optimal flow pathways**
- **low pressure drop**
- **improved mass- and heat-transfer**
- **easy (in-situ) regeneration and cost-effective product removal**
- **overall greatly improved productivity per cubic meter of reactor volume**

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

3D printing process - 'direct write'



Highly viscous paste → Micro extrusion through nozzle → Computer controlled deposition in x,y,z → Drying → Thermal treatment

Offers bespoke patterning of all-in-one structures in a variety of materials:

- **oxide ceramics (e.g. Al_2O_3, SiO_2, ZrO_2, CeO_2, mixed metal oxides, nanocomposites)**
- **metals (e.g. titanium, copper, aluminium, silver) and alloys (e.g. stainless steel)**
- **non-oxide ceramics (e.g. silicon carbide, carbon, boron nitrate)**
- **other functional materials: zeolites, polymers, MOFs, graphene oxide**

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

3D printed catalyst, adsorbents and reactor components at a glance

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

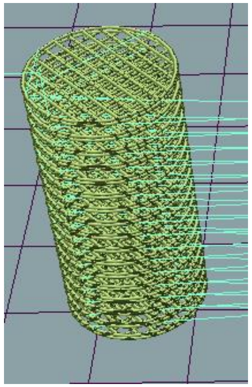
3D printed catalyst for DME production in CO2Fokus

CZA as-prepared

mixing the printing paste

calcination

CZA calcined



optimising the printing model

varying design and size

integration
into the reactor

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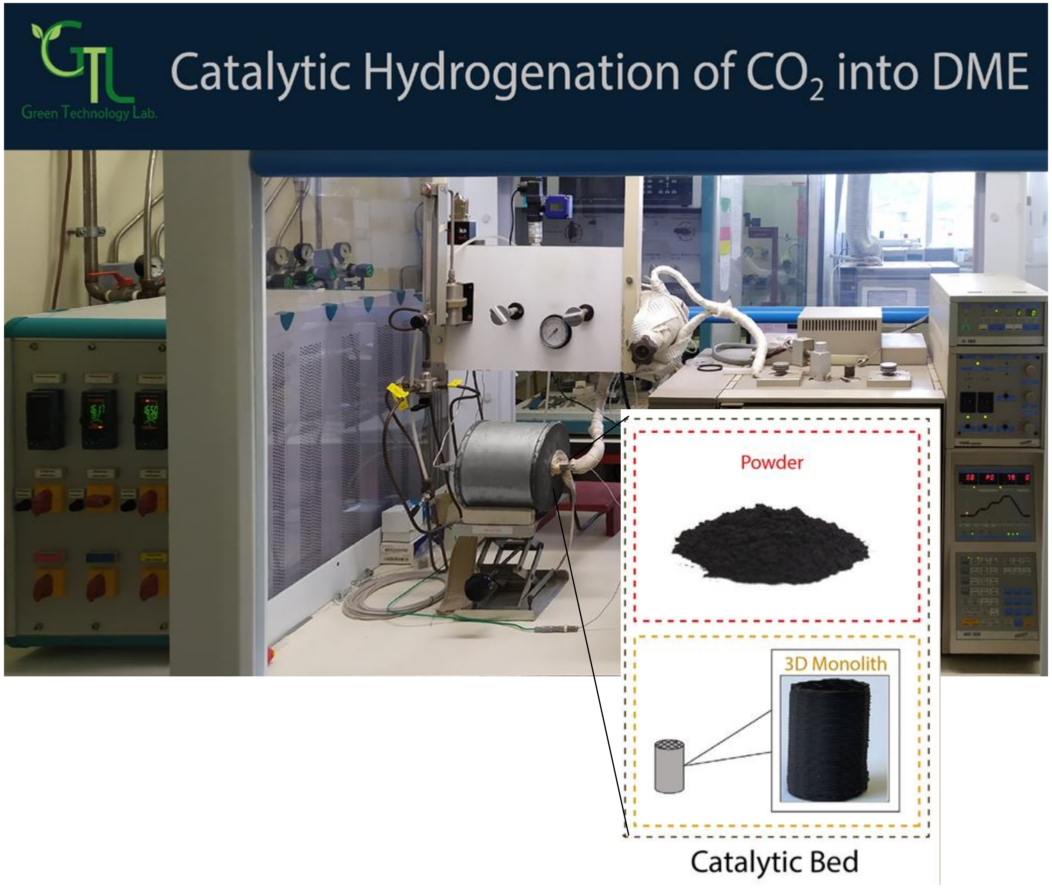
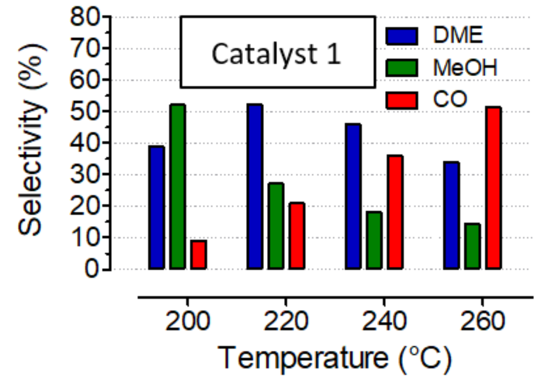
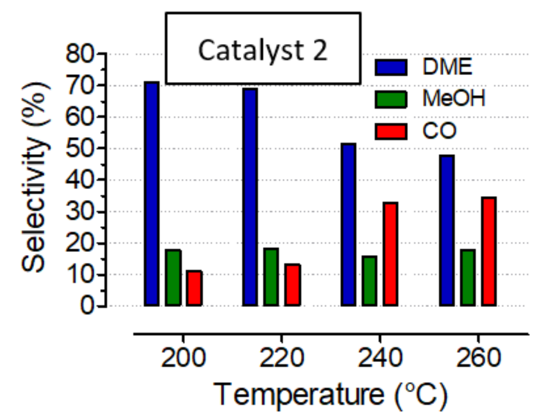
Single tube catalyst testing for DME production







For more details see further: Session 1B, Dr. G. Bonura
3D-printing in catalysis: Development of efficient hybrid systems for the direct hydrogenation of CO_2 to DME

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Multi-channel millireactors TRL4-TRL6

PROCESS INTENSIFICATION
↑↑↑ A/V

Characteristics required of the reactor:

- Improve the mass transference
- Optimisation of heat dissipation
- Dimensional uniformity of the tubes
- Thermal and mechanical stability
- Ease of handling

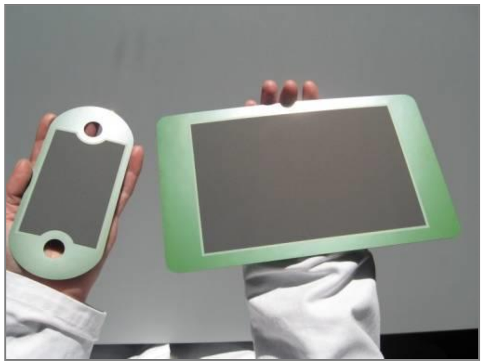
16 Millichannel Reactor				
Space velocity, $NL/kg_{cat}/h$	T, °C	CO_2 Conversion, %	DME Selectivity, %	DME Yield, %
	280	**12.1**	**31.0**	**3.7**

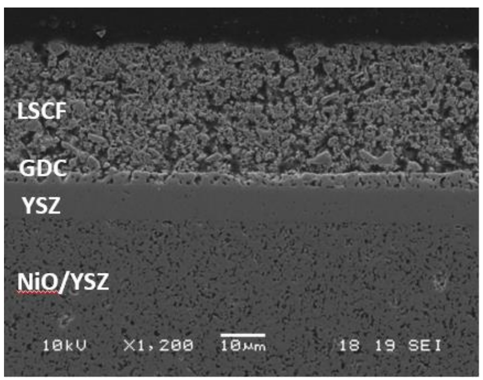
For more details see further: Session 3A, Dr. S. Perez
Process intensification in the conversion of CO2 with a milli-structured reactor

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

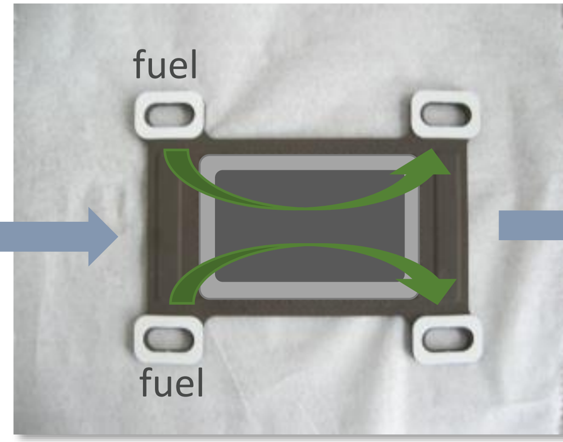
Solid oxide electrolyser cell and design, development and build up for H2 production

cell design

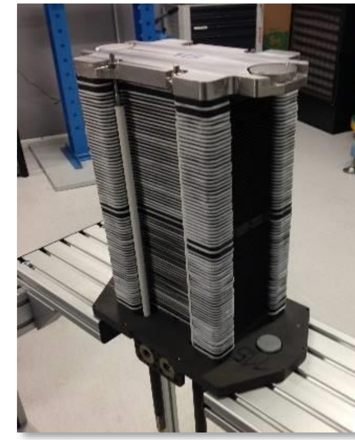




air



air



- Thin (ca. 250 µm) anode support with GDC/LSCF cathode
- Low cost state-of-the-art materials
- High mechanical strength and reliability

performances	unit	nominal
Conversion	%	60
H_2 Production	Nl	0.30-0.32
Stack power DC	kW	4.5
Thermal cycling	-	100-200

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Process design of CO2Fokus prototype demonstration units and on site integration

Reactor and SOE units will be integrated into existing carbon-intensive industrial facilities for on-site recycling of CO_2

Key Performance Indicators (KPI)	State-of-the-art	CO2Fokus
Energy efficiency (MJ/ton) DME	2300#	20-30% reduction
Catalyst & reactor design	TRL 3-4	TRL 6
Catalyst durability (hrs)	10^2	10^3
Pressure (bar)	30-70	30
Temperature (°C)	280	250
CO_2/H_2 feed (N L/h)	33/100	500/1500 or larger by numbering tubes
DME yield (%)	20-25	>30 (multichannel reactor)
CO_2 conversion (%)	30	>30
Overall H_2 conversion (%)	50	50

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Conclusions

Advance beyond the state-of-the-art

- Effective controlled deposition of active catalyst particles
- Reactor design: large surface to volume ratio and controlled macrostructure;

  millichannel reactors offer enhanced mass and heat transfer and 10-20% increase in reaction performance
- Integration and operation at Petkim's facilities - industrial CO_2 point source

Technical acceptance enablers

- Tackle potential technological and industries' concerns
- Provide technical guidelines for companies based on CO2Fokus demo design
- Tasks are put in place to provide analysis of environmental, financial and regulatory requirements
- Join forces with other projects on common interest topics to amplify the impact of our activities

Thank you!

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

vesna.middelkoop@vito.be

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

The KEROGREEN CO_2 plasma route to CO and alternative fuels

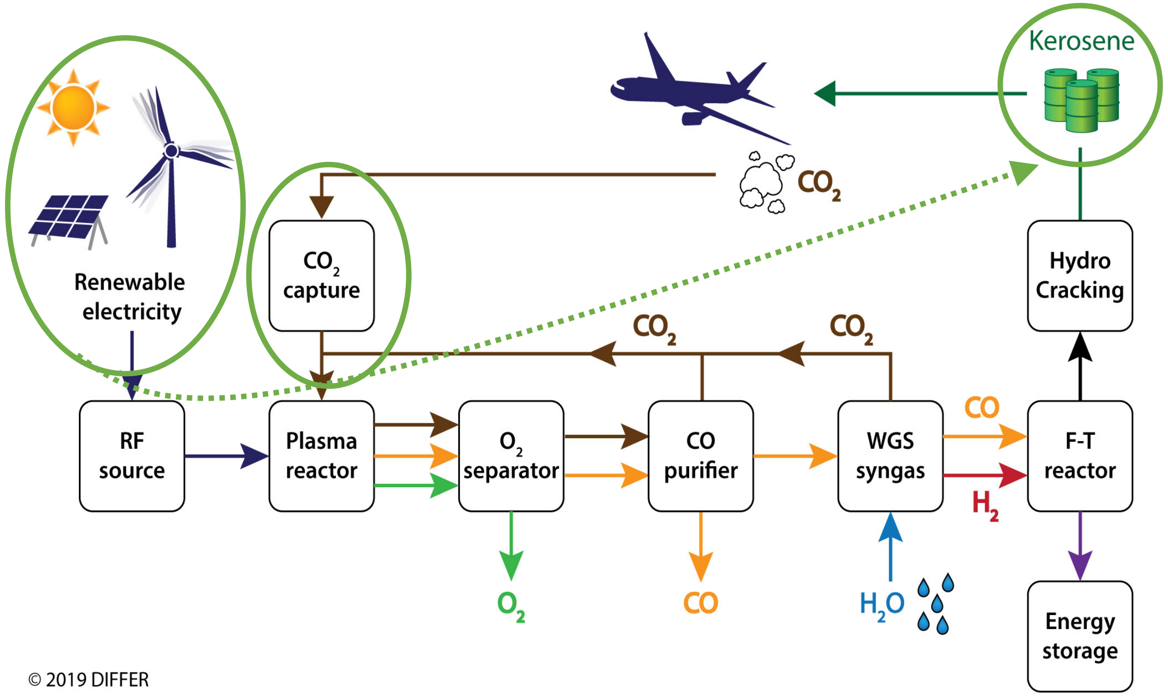
A. Pandiyan, S. Welzel, A. Goede, M.C.M. van de Sanden, M.N. Tsampas

DUTCH INSTITUTE FOR FUNDAMENTAL ENERGY RESEARCH, EINDHOVEN, THE NETHERLANDS

CCU and AltFuel workshop, 16-17 February 2021

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

Kerogreen project



© 2019 DIFFER

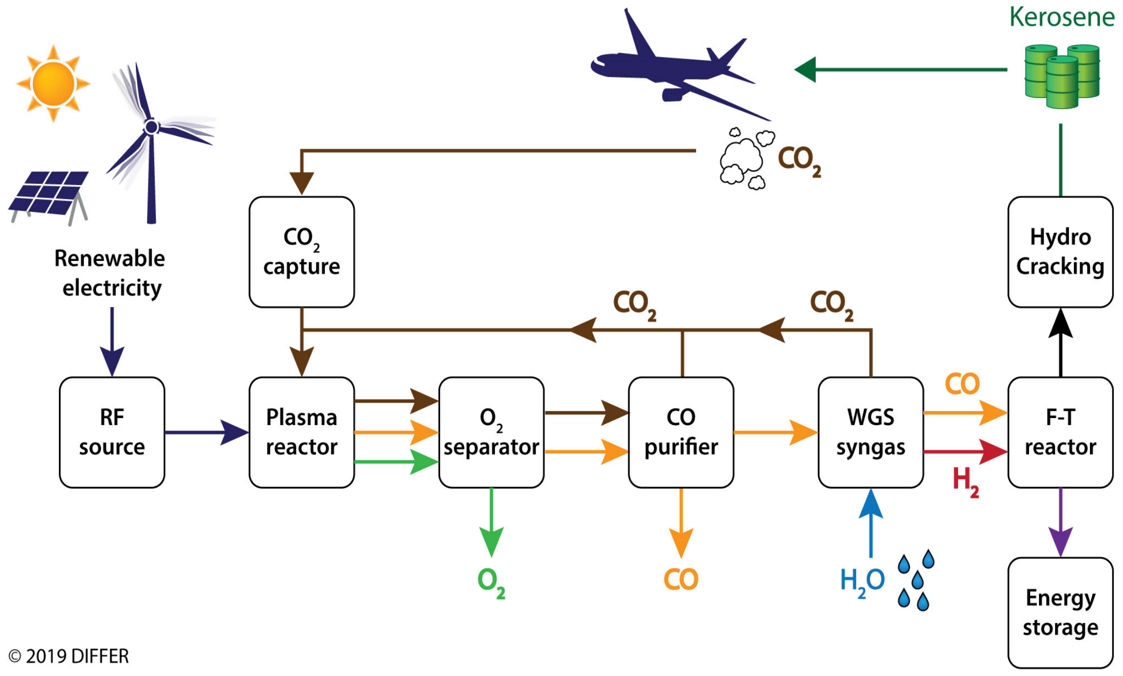
Kerogreen aim: Demonstation of the full chain process from renewable electricity, CO_2 (captured) and H_2O to kerosene.

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

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

Kerogreen project

DIFFER



KEROGREEN offers an innovative conversion route based on:

- CO_2 plasmolysis (DIFFER)
- Electrochemical O_2 separation (DIFFER, VITO, Cerpotech, Hygear)
- CO purification (HYGEAR)
- Water gas shift reaction reaction (KIT)
- Fischer-Tropsch synthesis (INERATEC)
- Heavy HC hydrocracking (KIT)

Main challenges

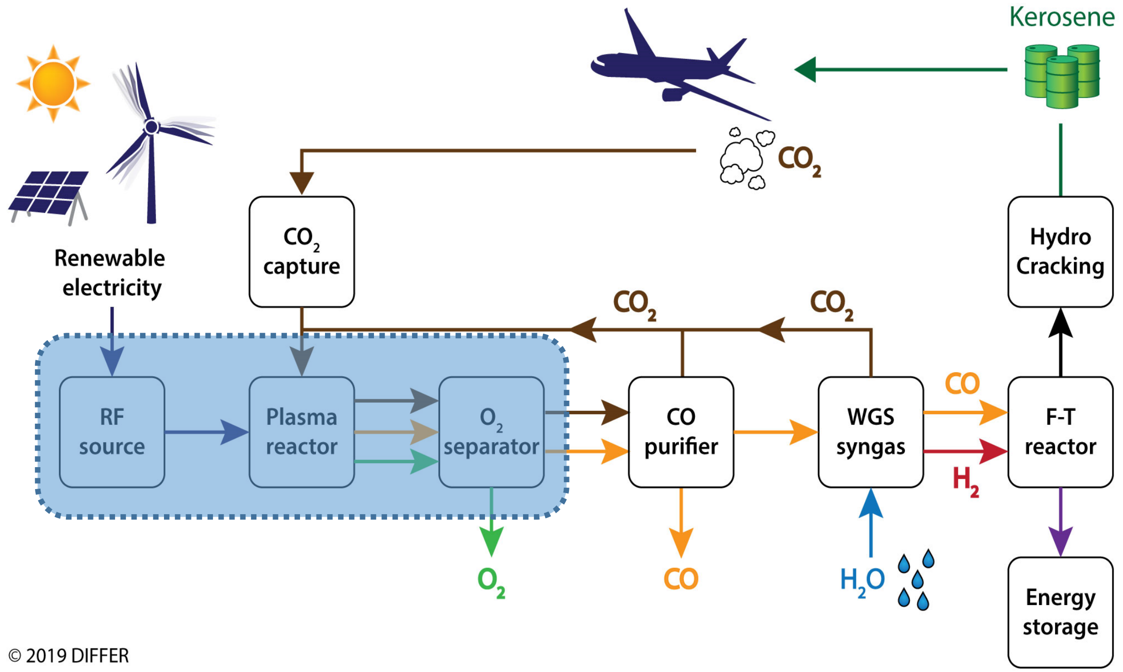
- Oxygen separation after plasmolysis by SOEC
- System integration of different technologies into one container sized assembly
- Maximization of the energy and carbon efficiency of the full chain

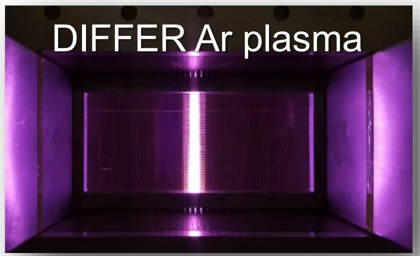
INERATEC

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

Kerogreen project

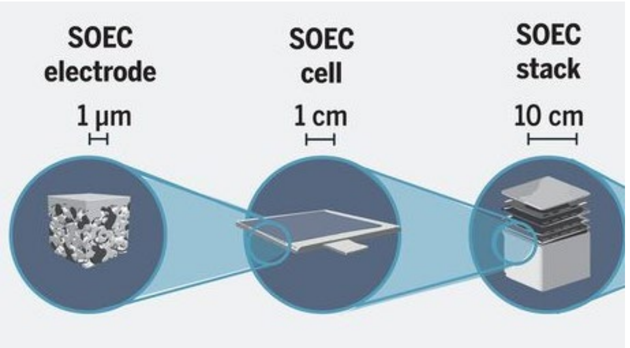
DIFFER





DIFFER involvement

- Plasmolysis
  - Plasma modeling and optimization
  - Upscaling from 1 to 6 kW
- Electrochemical oxygen separation
  - Proof of concept
  - SOEC material requirements
  - Upscaling from 1W to 1.5 kW



SOEC: Solid oxide electrolyte cells

DOI: 10.1126/science.aba6118

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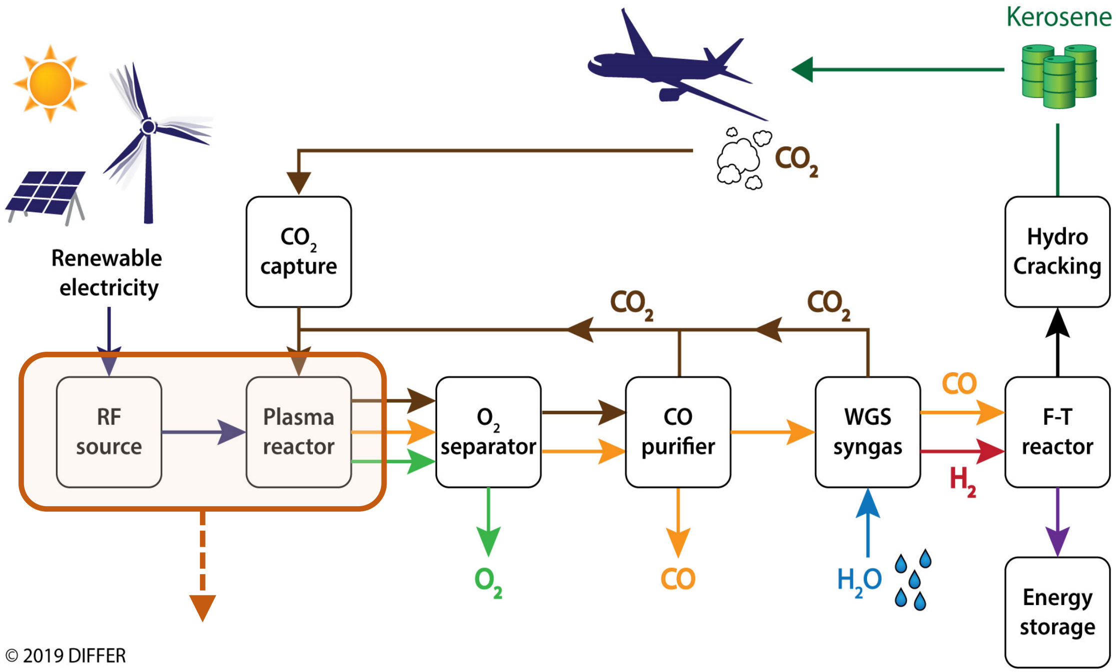
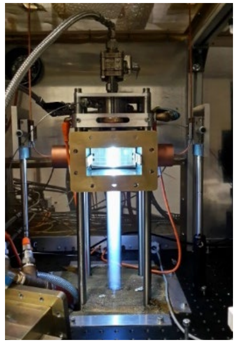
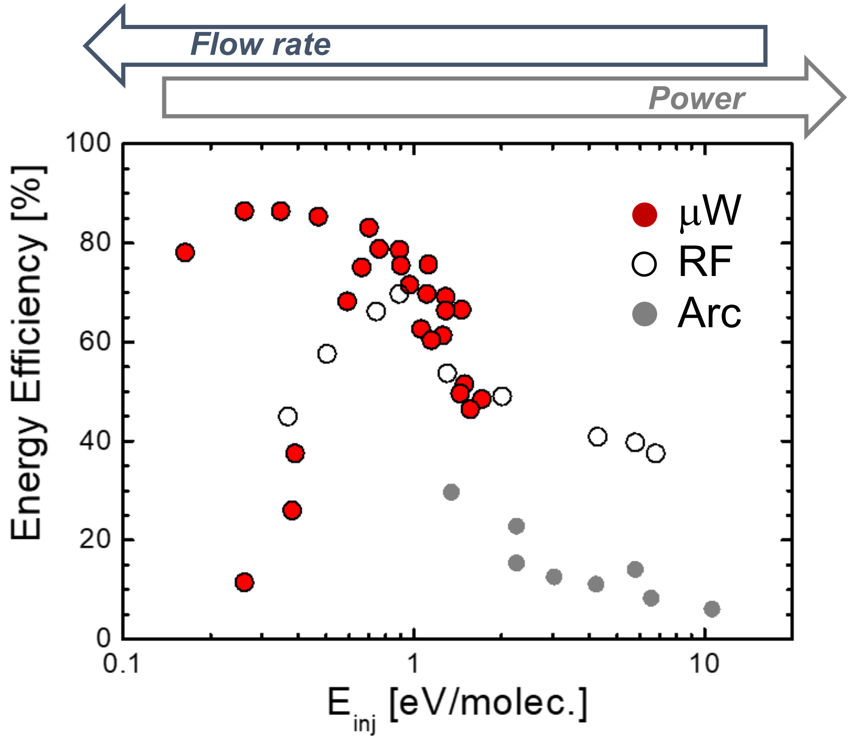
Why CO_2 plasmolysis?



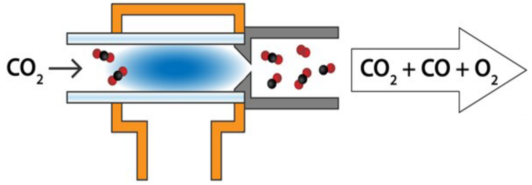


CO_2 plasmolysis: $2CO_2 \rightarrow 2CO + O_2$

- Input: CO_2 + renewable electricity
- Output: CO_2, CO and O_2
- High energy efficiency, …
- Main challenge O_2 separation



DOI: 10.1017/CBO9780511546075



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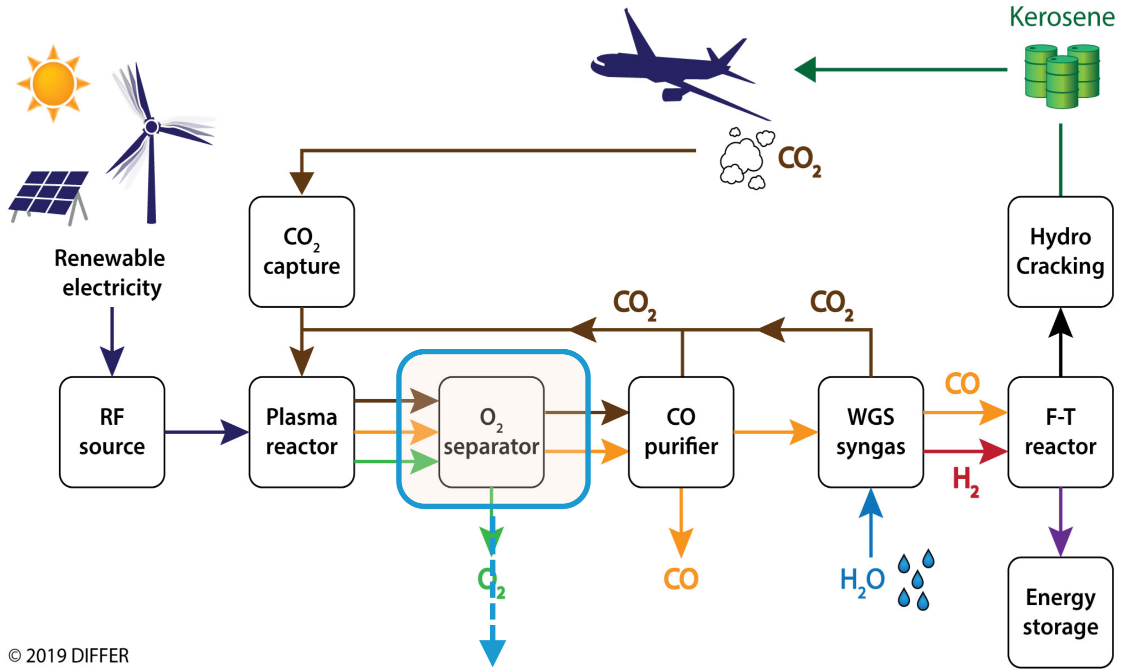
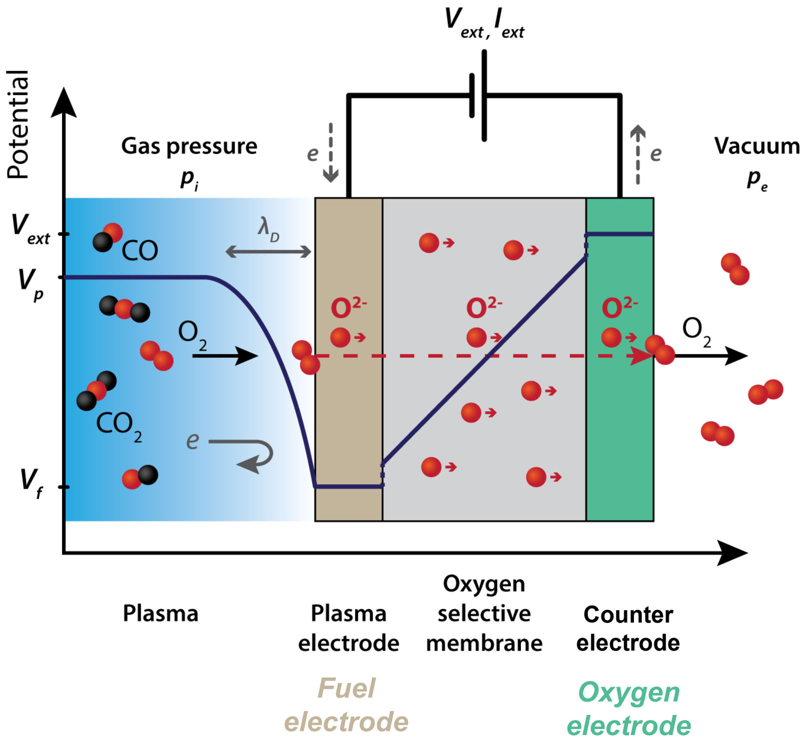
SOEC as oxygen separator



O_2 separation

- Difficult process
- Lack of literature
- SOEC: Electrochemical O_2 pumping



Conceptual design of plasma integrated SOEC

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

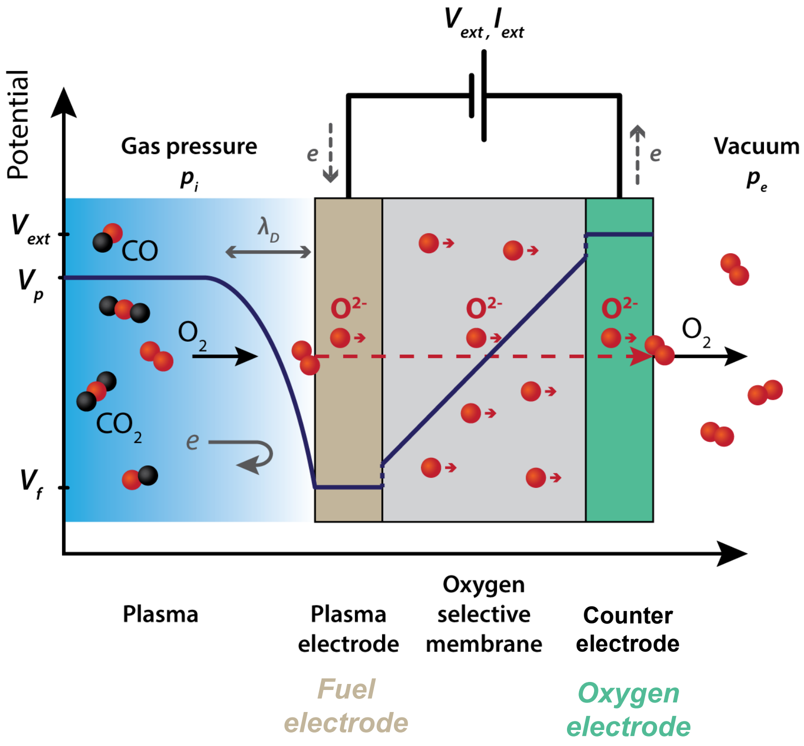
SOEC as oxygen separator

DIFFER

Material functionalities

- **For both electrodes:**
  - *Mixed electronic & ionic conductivity*
  - *Low overpotential losses*
- **Electrolyte**
  - *Oxygen ion conductivity*
  - *Low resistance → thin*
- **Key performance indicators**
  - *High oxygen fluxes*
  - *Stability*

- **<u>Plasma (or fuel) electrode</u>**
  - *Unconventional mixture (CO_2,CO,O_2)*
  - *Low CO oxidation activity*



Conceptual design of plasma integrated SOEC

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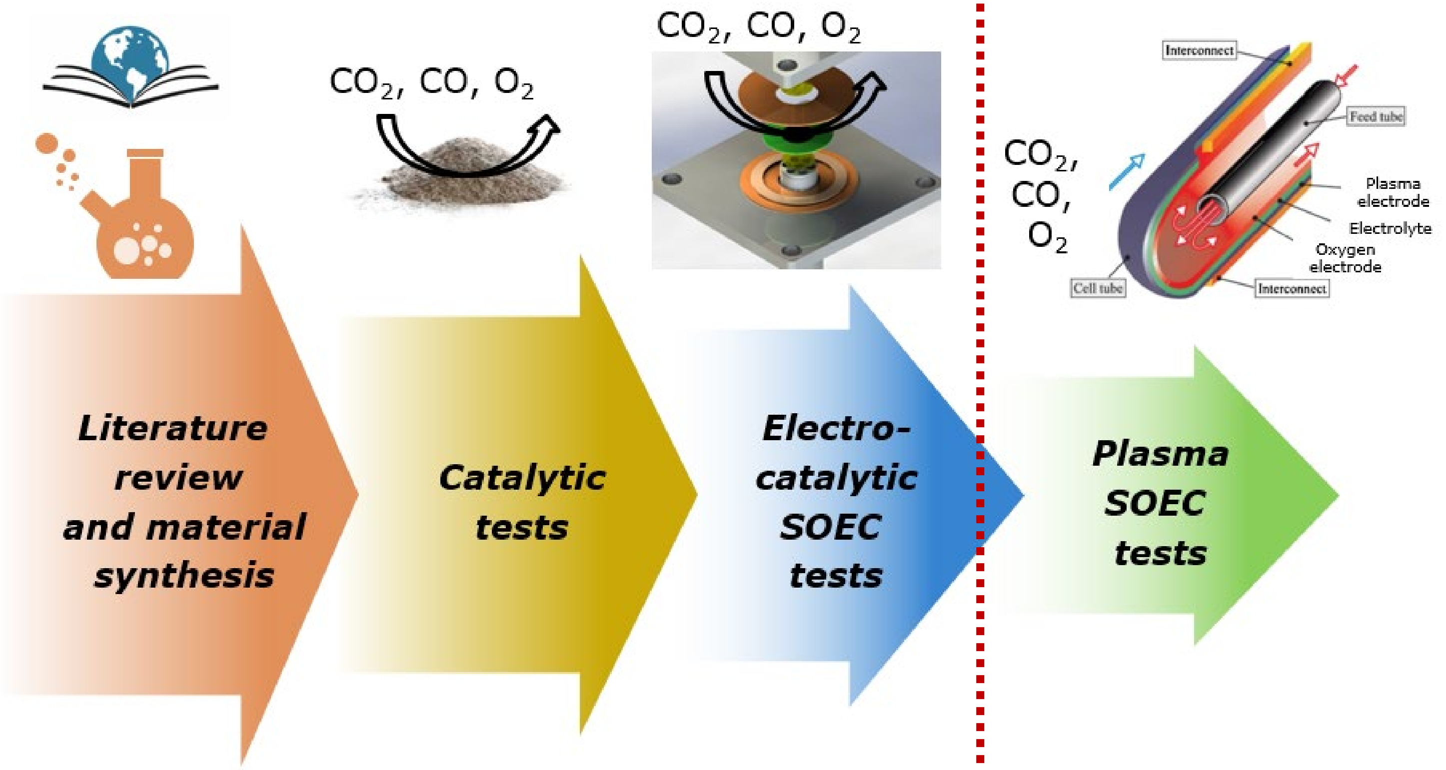
Material screening

Plasma electrode development

- Literature review (redox properties)
- Material synthesis (Cerpotech)
- Catalytic tests

Testing

- SOEC electrocatalytic tests
- Plasma SOEC integrated tests



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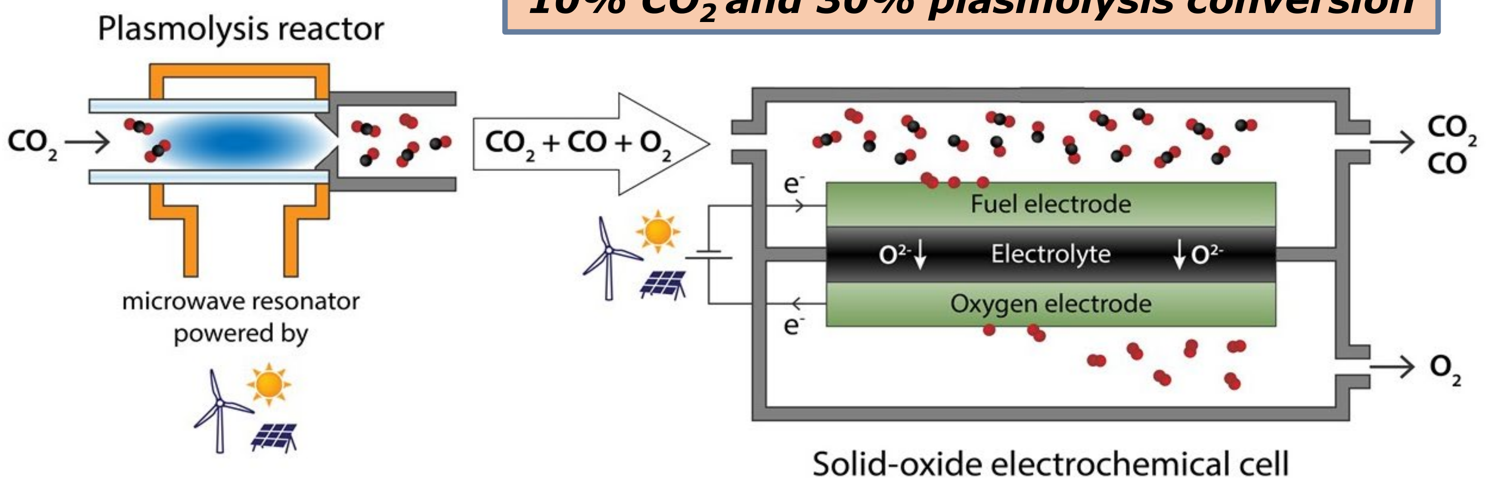
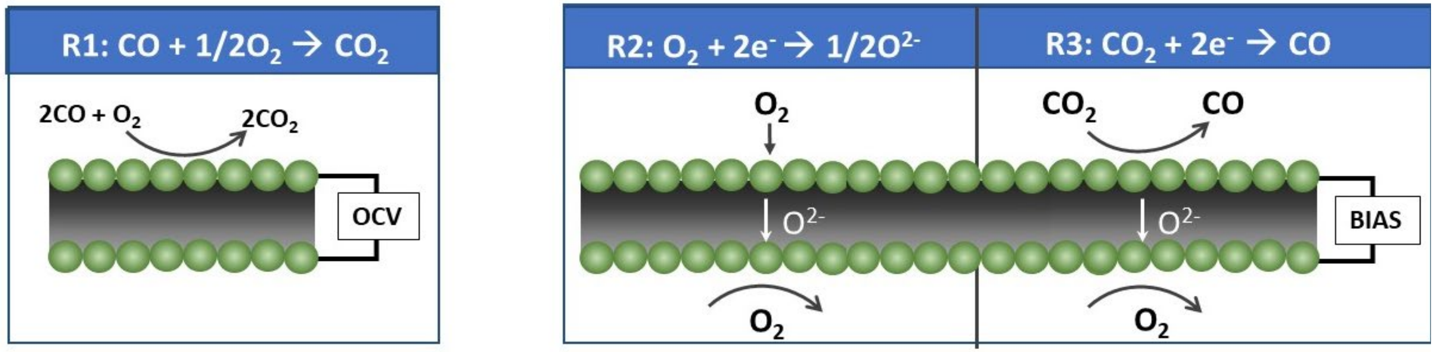
SOEC testing: Possible reactions

CO_2 plasmolysis equivalent gas mixture

10% CO_2 and 30% plasmolysis conversion





Unwanted ***Desired*** ***"Neutral"***

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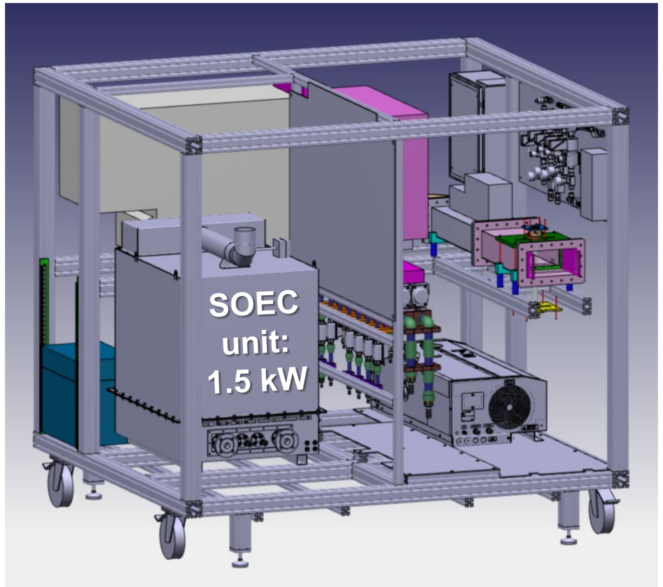
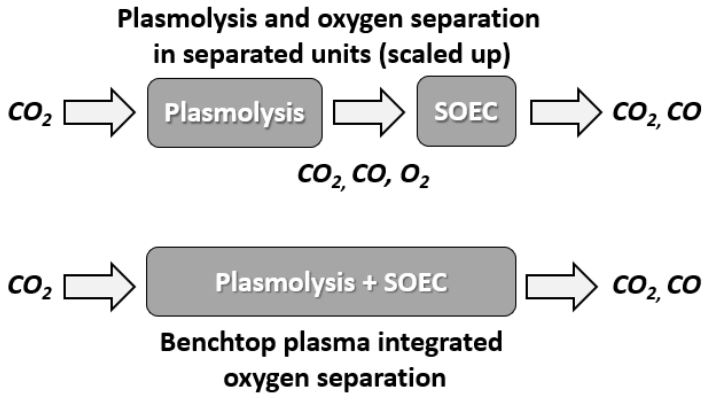
Summary and outlook

DIFFER

Summary

- Oxygen separation from CO_2 plasmolysis equivalent mixtures has been demonstrated.
- Lowering operating temperature decreases CO oxidation losses but also oxygen separation.
- SOEC operation with CO_2 plasmolysis equivalent mixtures improves materials stability.





Outlook for integration phase

- Advance SOEC architectures will decreased ohmic losses:
  - allow operation at lower T (less CO losses),
  - while achieving high oxygen pumping rates.
- Integrated phase: Commercial vendor → 1.5 kW unit
- DIFFER studies: CO_2 plasma-integrated SOEC.

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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

CO2FOKUS
ADVANCING CO_2 CONVERSION

CO_2 utilisation focused on market relevant dimethyl ether production, via 3D printed reactor- and solid oxide cell based technologies

3D-printing in catalysis: Development of efficient hybrid systems for the direct hydrogenation of CO_2 to DME

INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILISATION

Giuseppe Bonura

16 February 2021

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

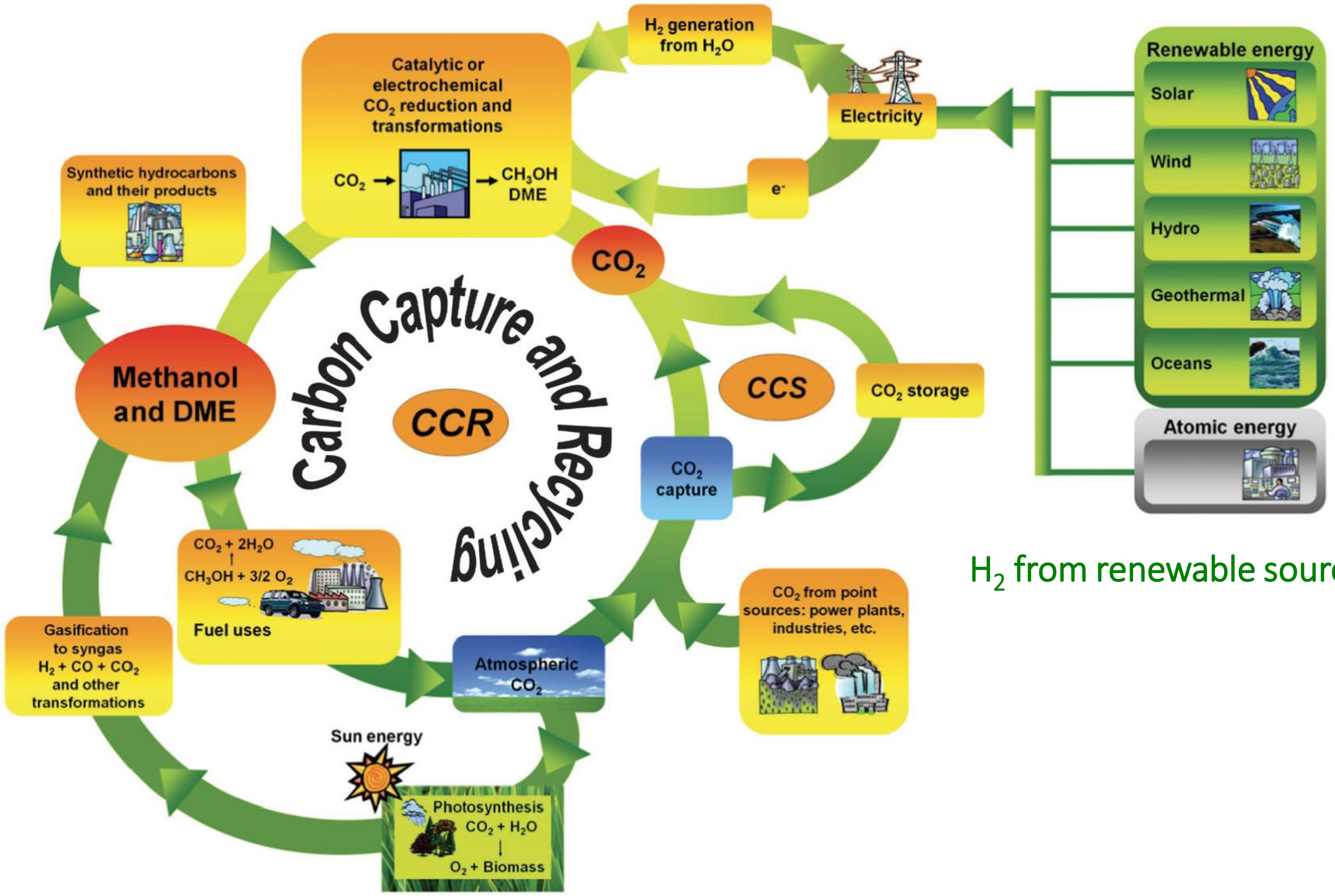
The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Overview

- Carbon Capture and Recycling
- DME: a multipurpose chemical & a fuel
- Conventional two-step processes
- Integrated one-step hydrogenation CO_2-to-DME
- 3D catalysis: a step forward
- Catalytic results
- Rationalization of the catalytic behaviour
- Conclusions

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

CO_2 as a substitute for toxic CO, derived from fossil carbon

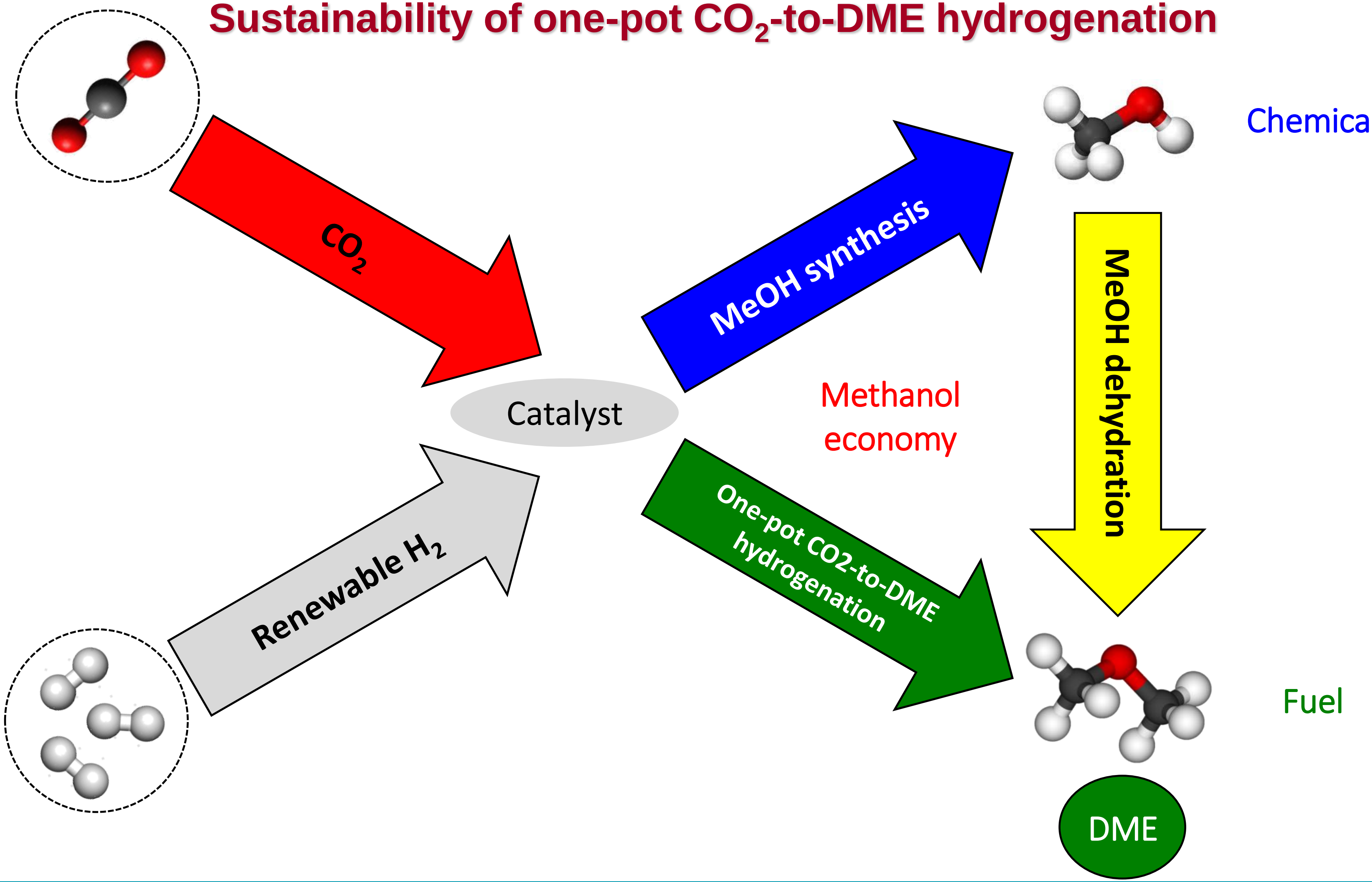


H_2 from renewable sources

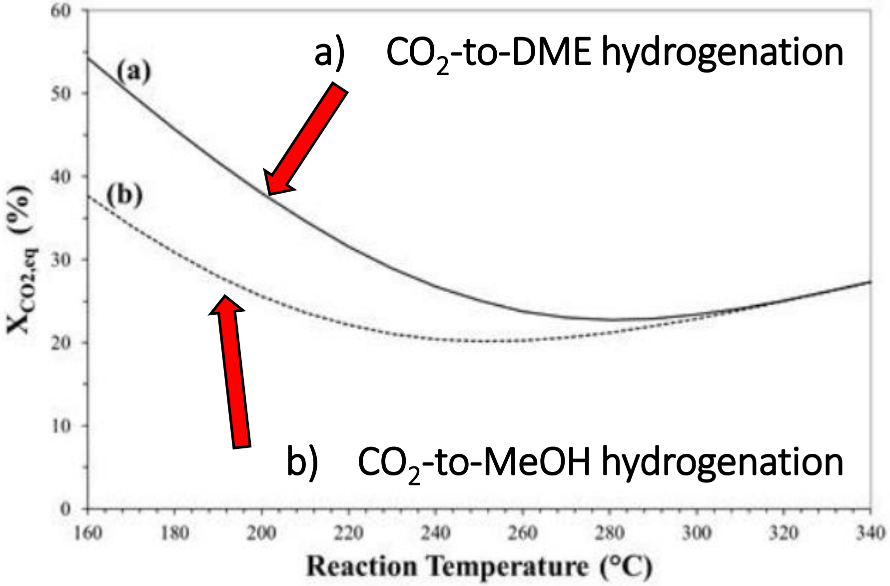
Olah et al.// Chem. Soc. Rev. 43 (2014) 7995

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Sustainability of one-pot CO_2-to-DME hydrogenation



Thermodynamics of CO_2 hydrogenation



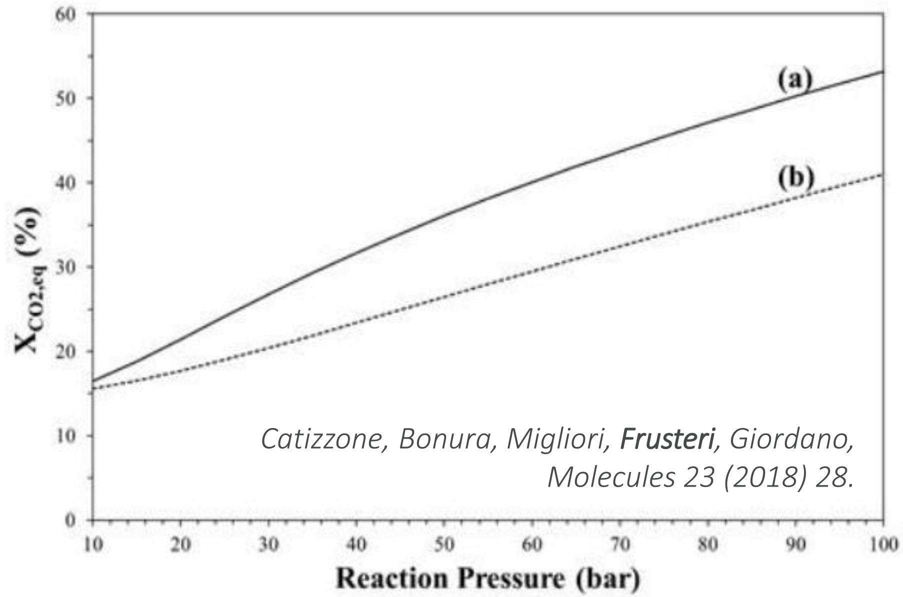
$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \qquad \Delta\tilde{H}_R^\circ = -49.4kJ \cdot (mol_{MetOH})^{-1}$$

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad \Delta\tilde{H}_R^\circ = +41.2kJ \cdot (mol)^{-1}$$

$$\boxed{2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O \qquad \Delta\tilde{H}_R^\circ = -24kJ \cdot (mol_{DME})^{-1}}$$

$$CO + 2H_2 \Leftrightarrow CH_3OH \qquad \Delta\tilde{H}_R^\circ = -90kJ \cdot (mol_{MetOH})^{-1}$$

$$2CO_2 + 6H_2 \Leftrightarrow CH_3OCH_3 + 3H_2O \qquad \Delta\tilde{H}_R^\circ = -122kJ \cdot (mol_{DME})^{-1}$$



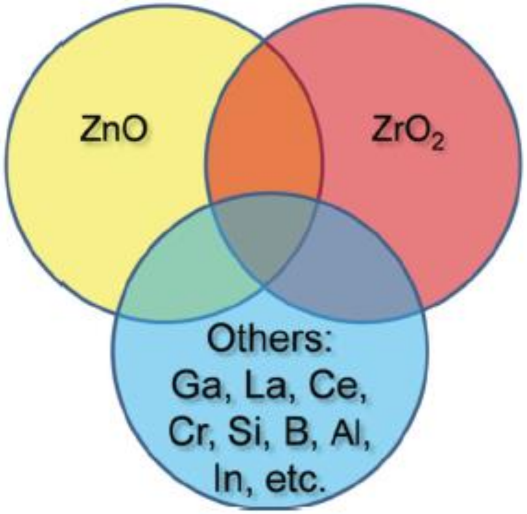
*Catizzone, Bonura, Migliori, **Frusteri**, Giordano, Molecules 23 (2018) 28.*

Due to methanol consumption by dehydration reaction, **the one-step process is more efficient than the two-step process**, with a main benefit at low temperature and high pressure.

Conventional two-step processes

1. Methanol synthesis from syngas

Cu-based catalysts (high activity and selectivity)



- Catalyst composition
  - a) Support ⇒
    - High SA_{BET}
    - Cu^+ stabilization
  - a) Promoter ⇒
    - High MSA_{Cu} and D (%)
    - High Poisoning resistance

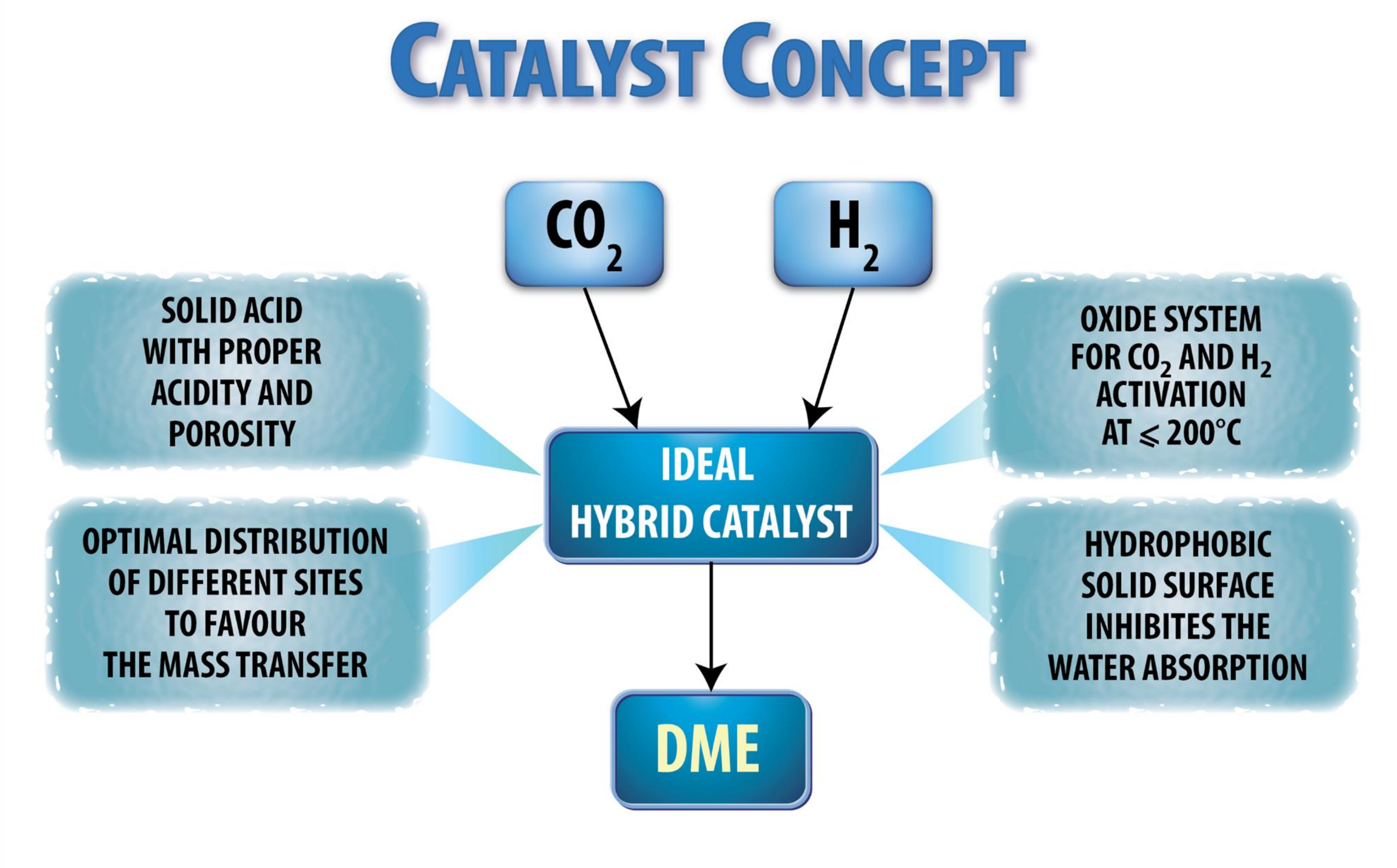
OPEN ISSUES
a) Metal/Support interaction
b) Metallic Dispersion
c) "Water Poisoning"
d) REACTION MECHANISM

- Catalyst preparation
  - Co-precipitation [Jingfa *et al.*, 1996]
  - Sol-Gel [Köppel *et al.*, 1998]
  - Incipient-Wetness [Toyir *et al.*, 2001]
  - Combustion [Arena *et al.*, 2004]
  - Reverse coprecipitation under ultrasounds [Arena *et al.*, 2007]
  - Gel-oxalate coprecipitation [Bonura *et al.*, 2014]

2. Dehydration of methanol

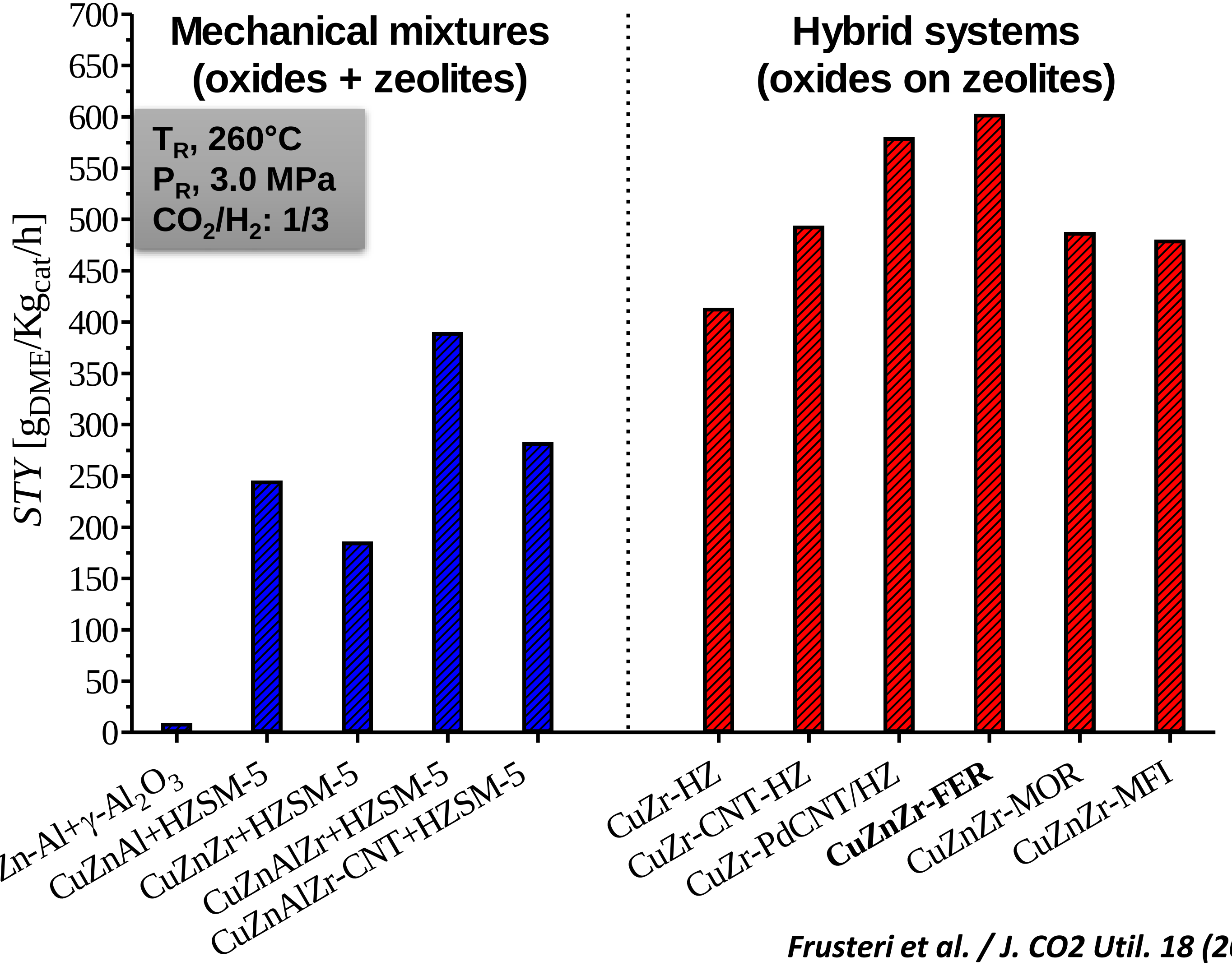
γ-Al_2O_3, zeolites, heteropolyacids, …

Integrated one-step process: new hybrid catalysts



Frusteri *et al.* // *Catal. Today* 277 (2016) 48–54.
Frusteri *et al.* //*Catal. Today* 281 (2017) 337–344.

Mechanical Mixtures vs. Single Grain Hybrid Systems



Frusteri et al. / J. CO2 Util. 18 (2017) 353–361

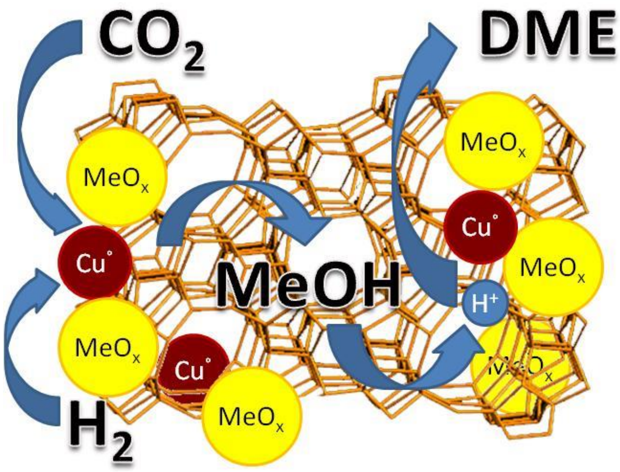
The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Integrated one-step process: new 3D hybrid catalysts

Preparation of 3D hybrid catalysts with reproducible properties at long radius

Combination of metal/oxide(s) and acidic functionalities in a single solid system

The parent catalysts are not distinguishable anymore



3D printing (VITO)

Coprecipitation of metal precursors by oxalic acid in a slurry solution containing a finely dispersed zeolite / binder paste / printing /drying / calcination

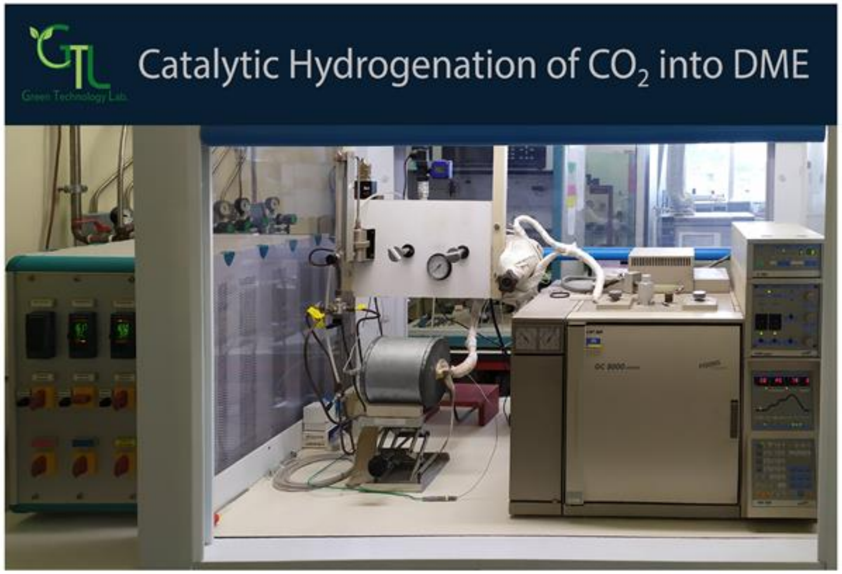
Not only uniform distribution…
exposure *vs.* accessibility of surface sites

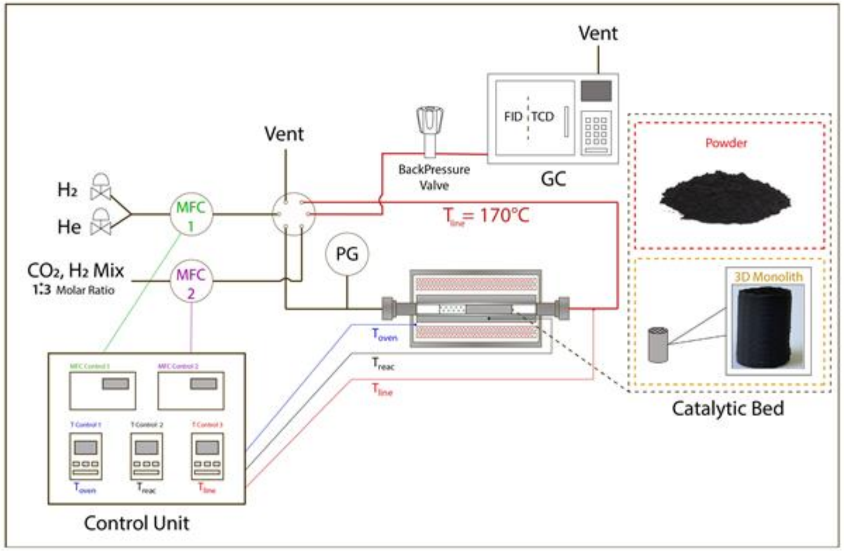
- Reproducibility
- Properties controlled
  - Texture
  - Structure
  - Morphology
  - Surface

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Experimental setup

CO_2-to-DME hydrogenation
Reactor id: 4.0 mm
wt_{cat}=0.25 g
H_2:CO_2:N_2 = 69:23:8
GHSV: 8,800 $ml_n/g_{cat}/h$
P_R=30 bar
T_R=200-260 °C





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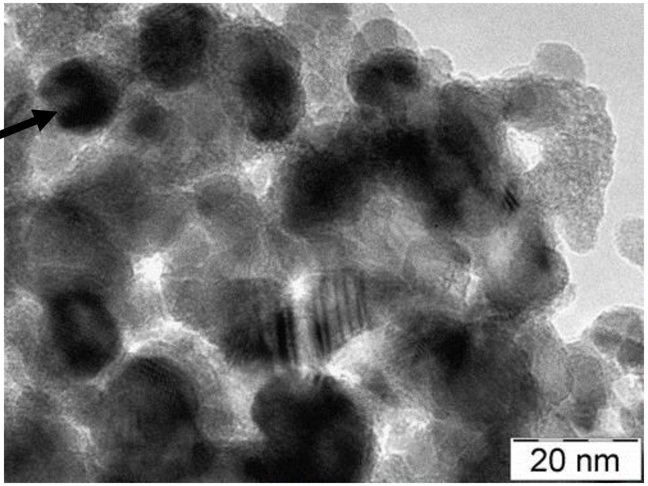
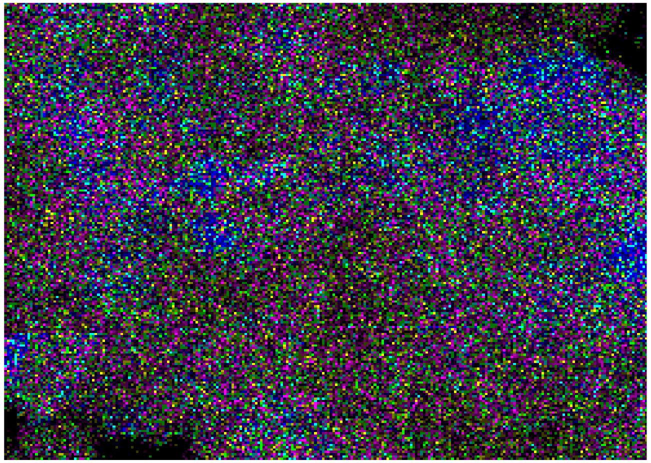
Synthesis of a 3D hybrid catalyst

Cu phase



Coprecipitation of metal precursors by oxalic acid in a slurry solution containing the solid acid carrier

3D catalyst



Very good homogeneity of metal precursors, with long-range distribution of elements per unit of acidi surface.

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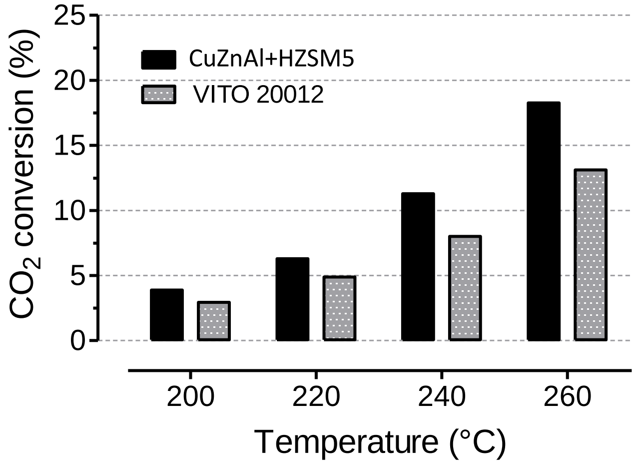
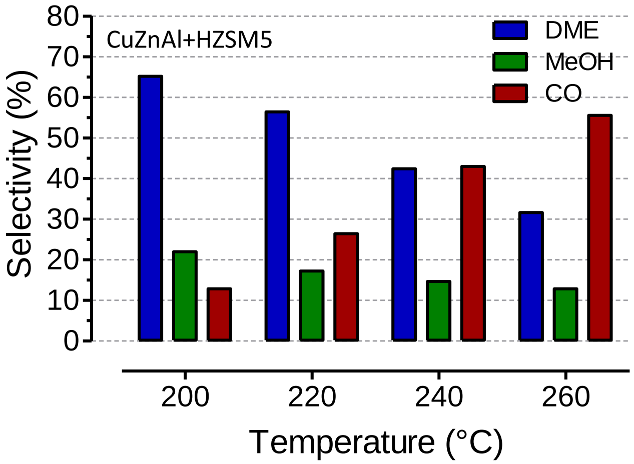
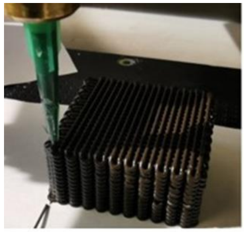
Conventional powdered vs. 3D printed catalysts (VITO)

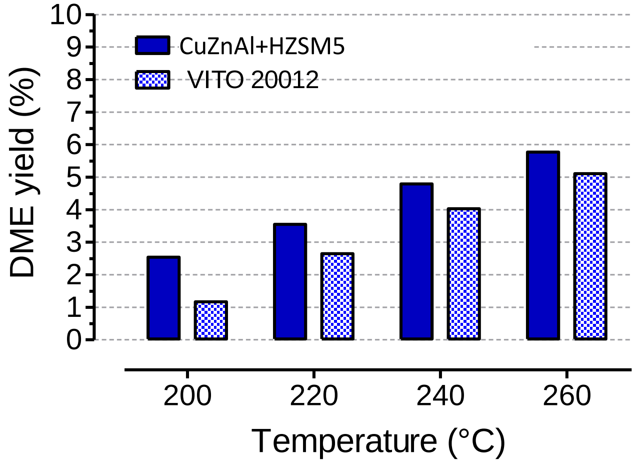


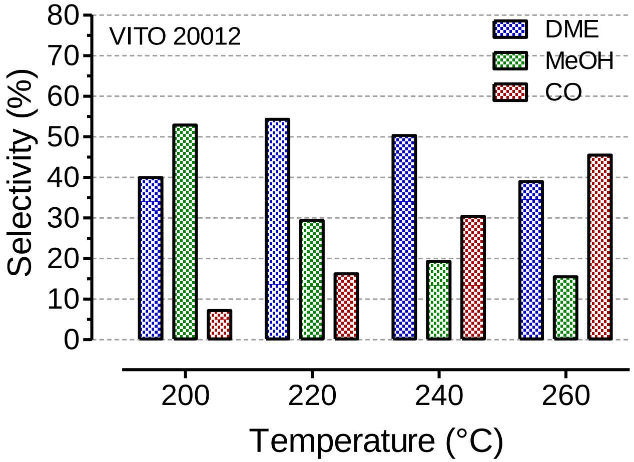


Conventional catalyst exhibits a better performance than the 3D printed crushed monolith

20012







Selectivity pattern quite different between conventional and 3D catalyst

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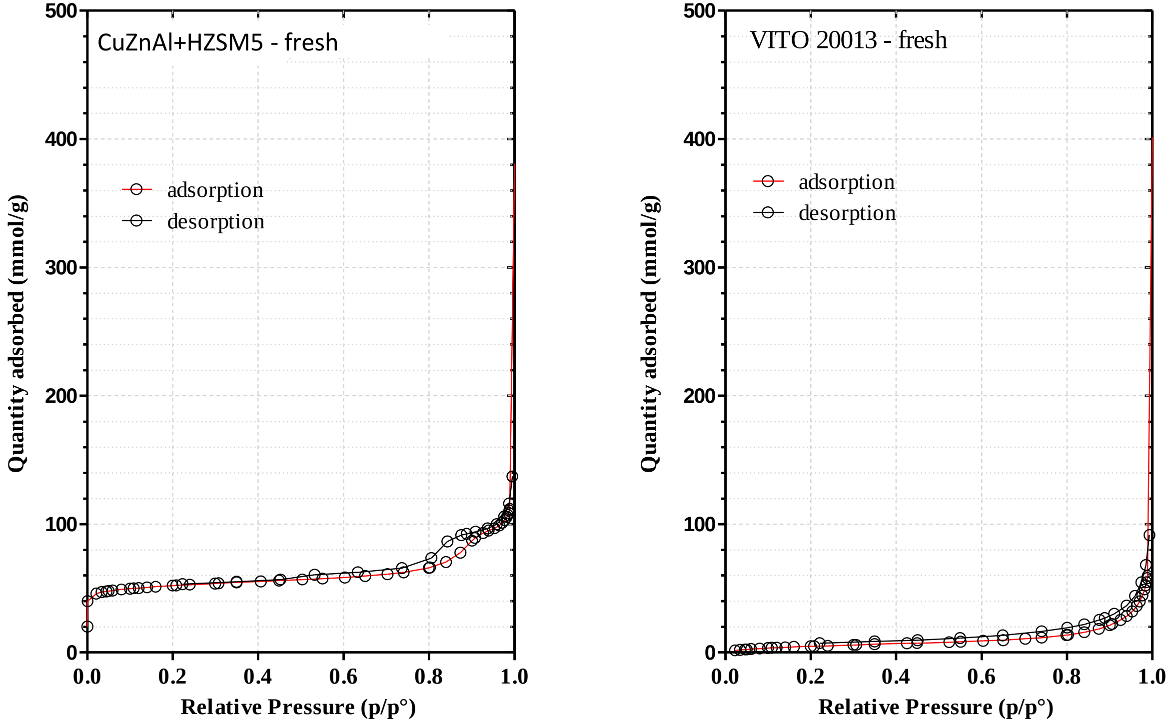
Textural properties

A lower activity of the 3D catalysts is mainly ascribable to a dramatic loss of microporosity during printing

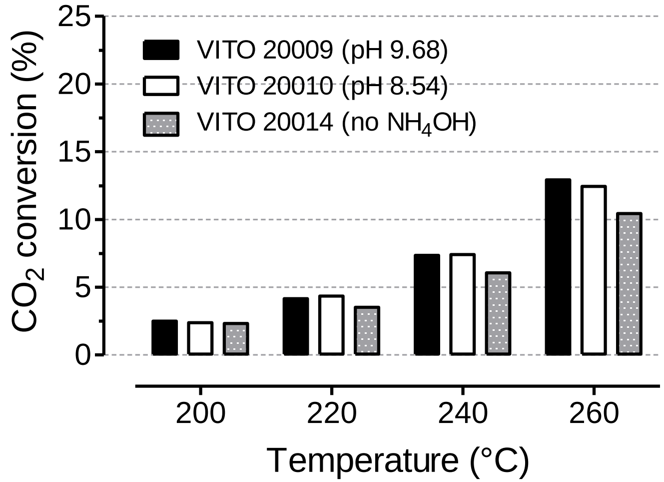
SAMPLE	SA_{Lang} (m^2/g) (a)	PV (cm^3/g) (b)	MV (cm^3/g) (c)	APD (Å) (d)
CZA+HZSM5 - fresh	233.3±1.5	0.146	0.081	25
VITO 20013 - fresh	30.5±1.2	0.140	0.008	184
VITO 20013 - used*	175.6±1.5	0.173	0.060	39

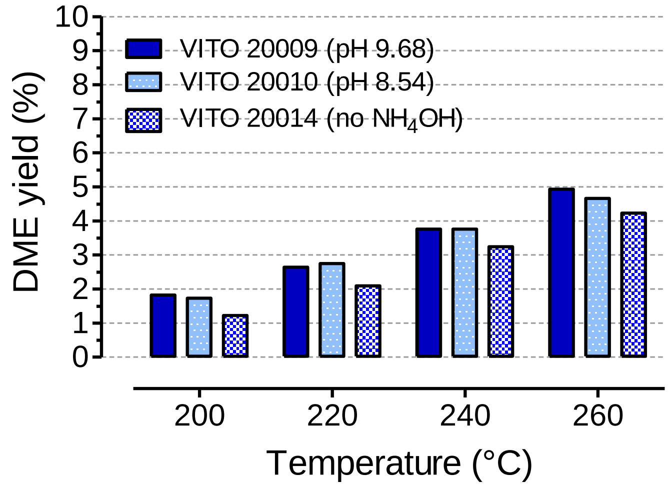
*Sample recovered after run at 30 bar and 260 °C, upon cooling at r.t.
(a) Surface area determined according to the Langmuir model
(b) BJH desorption cumulative pore volume
(c) Micropore volume from Horvath-Kawazoe at relative pressure ≈ 0.2
(d) Average pore diameter determined from the geometrical formula: 4PV/SA

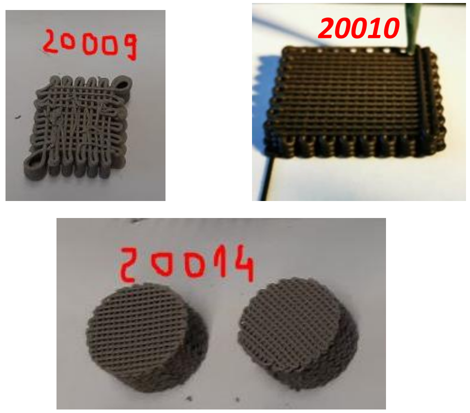


The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

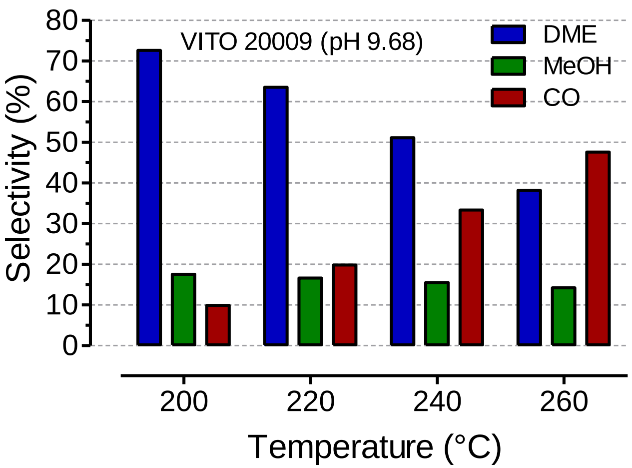
Influence of pH on 3D printing

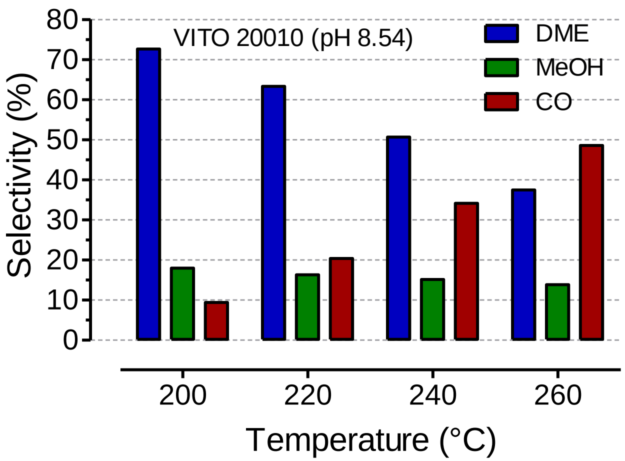


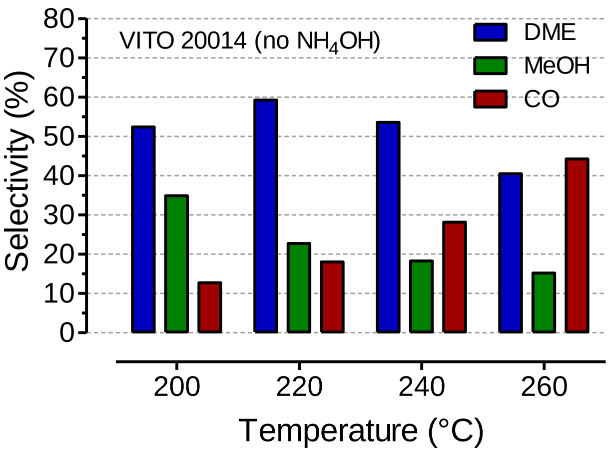




The preparation of the paste for 3D printing benefits from a higher pH



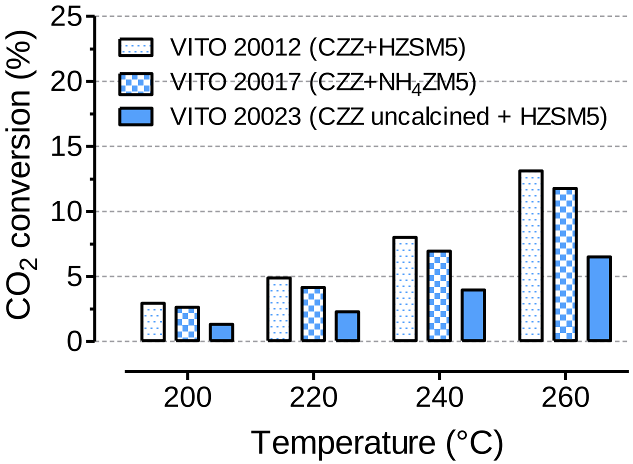


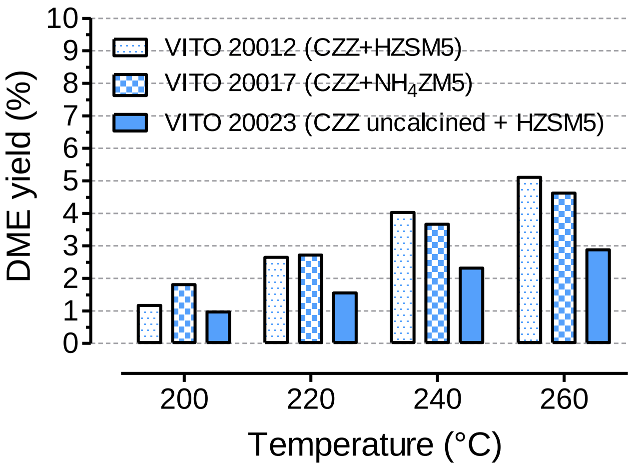


The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Influence of pre-calcination of the phases :

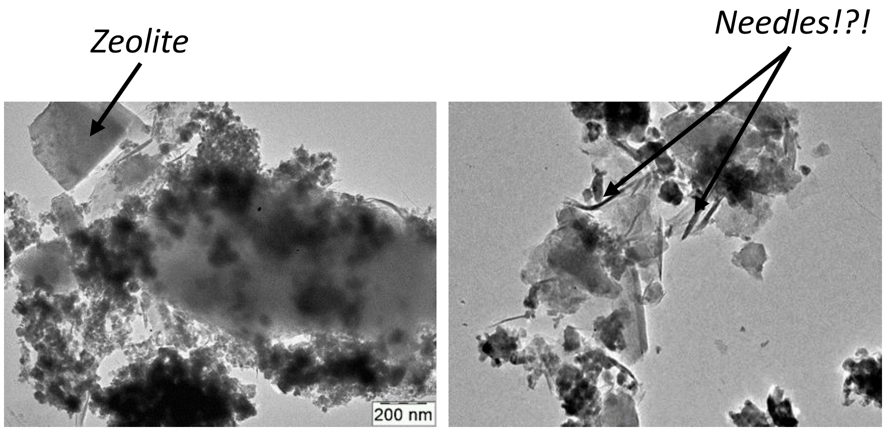
VITO 20012 (precalcined phases before printing) *vs.* VITO 20017 (CZZ+ NH_4ZSM-5, co-catalyst not calcined) *vs.* VITO 20023 (CZZ uncalcined + HZSM-5)





1. On VITO 20017, printing before stabilization of the zeolite phase prevents the shift of equilibrium as the result of a significant inhibition or reduction of acid sites (NH_3-TPD !), not available/activable anymore even after further calcination.
2. On VITO 20023, the activation of CO_2 is significantly depressed on a poor stabilized Cu phase (XRD!), demonstrating as the extent of metal-oxide interface during preparation/calcination is crucial for addressing catalytic behaviour.

20017



VITO 20017 – TEM images on the fresh sample (calcined at ITAE @ 500 °C)

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Key messages

- The development of a catalytic process for the direct conversion of CO_2 to DME with 3D hybrid systems is feasible.
- Very promising results were obtained using 3D hybrid system consisting of a mixed oxide phase supported on an acidic preformed carrier.
- 3D printing before stabilization of the acid phase prevents the shift of equilibrium as the result of a significant inhibition or reduction of acid sites, not available/activable anymore even after further calcination.
- 3D printing before calcination of methanol phase showed that the activation of CO_2 is significantly depressed on a poor stabilized metal phase, confirming as the extent of metal-oxide interface during preparation/calcination is crucial for addressing catalytic behaviour.
- High selectivity to DME can be achieved at reaction temperature lower than 250 °C and the current limit is related to CO_2 activation.

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Open Issues

- Novel active phase suitable to activate CO_2 at low temperature taking a direct advantage on DME selectivity (see thermodynamics)
- New binders for a full control of texture/structure/surface properties
- Innovative stacked and alternating 3D reactors for increasing DME productivity from CO_2 hydrogenation in one step
- Optimization of catalyst stability and regeneration

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Acknowledgements

CO2FOKUS
ADVANCING CO_2 CONVERSION

- EU H2020 - Grant agreement N. 838061 – CO2Fokus

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

http://www.itae.cnr.it

Dr. Francesco FRUSTERI

Dr. Catia CANNILLA

Mr. Aldo MEZZAPICA

Dr. Giuseppe BONURA

Dr. Serena TODARO

Dr. Leone FRUSTERI

Thank you!

The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061

Plenary session (chairperson Fausto Gallucci)	
14:00-15:00	Dr. Angels Orduna (Spire 2030)

Processes4Planet

Transforming the European Process Industry for a sustainable planet & a prosperous society

INTERNATIONAL WORKSHOP ON CO2 CAPTURE AND UTILIZATION

TU/E - EINDHOVEN

16 February 2021

WHO ARE WE

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

A vibrant community ...

A.SPIRE – European Cross-Sectoral association

10 Sectors

+20 EU Countries

+160 Members teaming up

DG R&I
DG Grow

COMMISSION EUROPÉENNE

- Industrial Associations &Clusters
  Industries, incl SME's, New Sectors ...
- RTO's & Higher Education Institutions
- Consultancies, NGO's,
  KIC's, Innovation Agencies, ...
- MS & Regional Representatives
  Financial Partners

OPEN APPROACH: inclusive of different stakeholders and welcoming Newcomers

PROCESS INDUSTRY: INDISPENSABLE

- **€ 1.8** turnover
- **4,7%** of EU 28 GDP
- **+ 25 million jobs** (direct & indirect)
- **+ €78 billion (CAPEX) investments** in the EU
- Crucial in **an exceptionally large number of value chains**
- Strongly resilient and **strategically key to relaunch the EU economy post-COVID19**

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

UNIQUE CROSS-SECTORIAL APPROACH

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

Accelerating Innovation and Maximising sustainable impact accross sectors and borders

- First Partnership ever gathering **8 Process Industry sectors. Currently 10**
- **Continuous dialogue on R&I and trust relation** across SPIRE sectors and beyond
- **Enhanced voice** to shape the framework of process innovation and competitiveness through the dialogue with the public sector

THE VOICE OF 10 SECTORS

JOINT SOLUTIONS

- **Collaboration** with the innovation ecosystem, the value chain, society and the public sectors (RTOs, NGOs, EC, MS, regions…)
- Development of **joint solutions** through **125 SPIRE projects** funded from **2014 to 2019**, always respecting the Intellectual Property

- Direct access to a **pool of knowledge, talent** and applied research services through the RTOs
- Direct access to specialised SME providers
- Direct access of **SMEs** to growth opportunities, customers and new markets

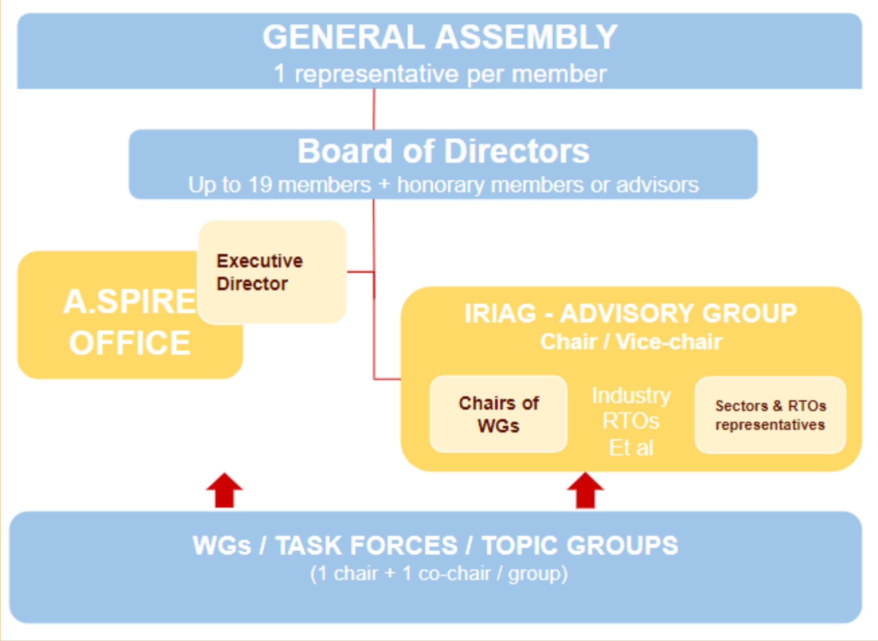
OPPORTUNITIES

GOVERNANCE SPIRE cPPP

PRIVATE PARTNER

ASSOCIATION SPIRE

- Discuss priorities
- Propose call topics
- Form consortia
- Apply to calls



PARTNERSHIP BOARD

- Discuss priorities & call topics H2020/HEU
- Assess progress

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

PUBLIC PARTNER

- Develop work programme
- Publish open calls

European Commission

TRENDS REPORT 2020 – SPIRE PROJECTS OUTCOMES

In 2014-2019 SPIRE cPPP has supported a total of **125 projects**.

1775

organisations participating in SPIRE granted projects

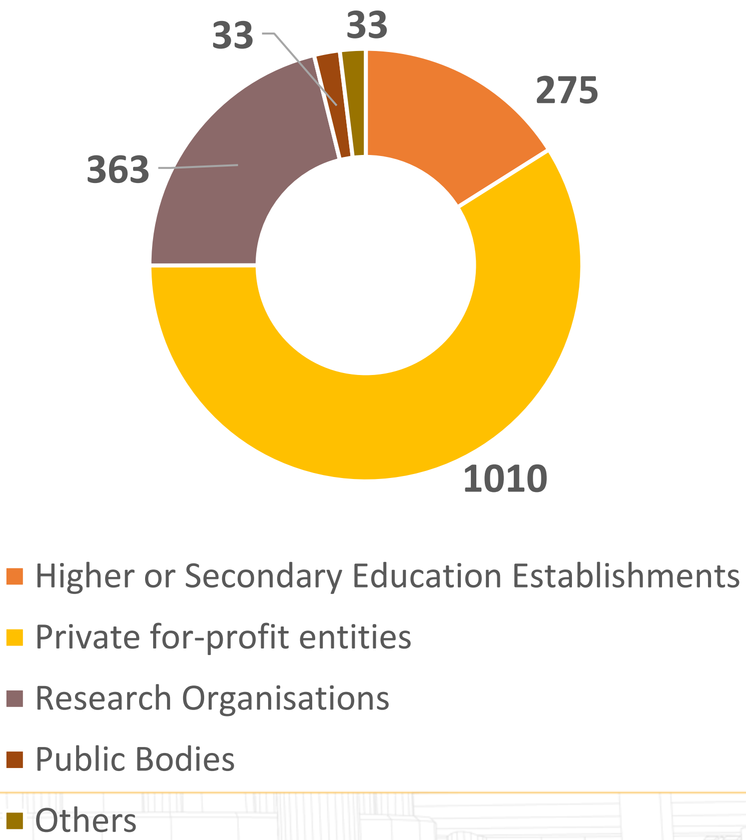
30%

of the participating organisations are **SME**s

EUR 205 million

EC contribution to SPIRE projects **SME participants**

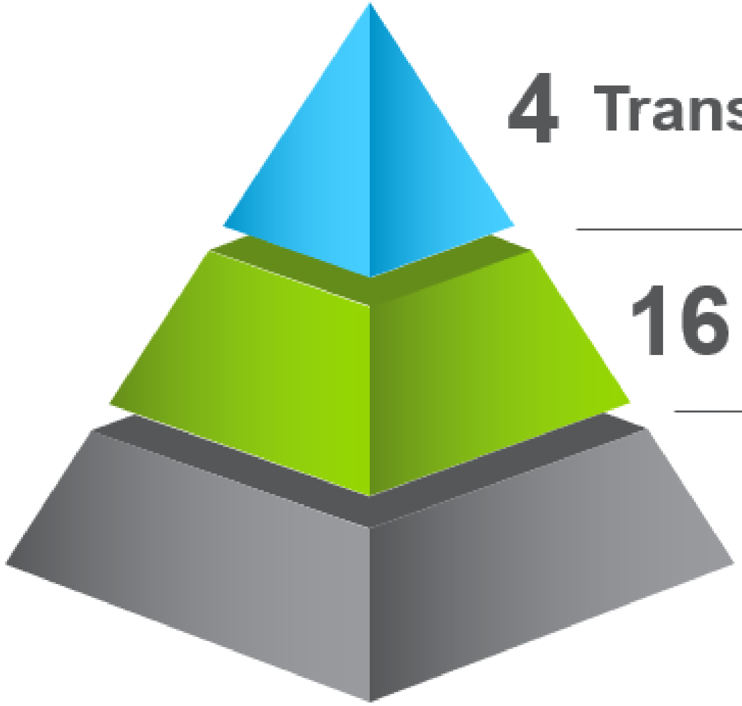
Organisations in granted projects per category



Processes4Planet Towards the Next Generation of EU Process Industry

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

Transformation levers and tools to enable P4Planet to achieve its ambitions



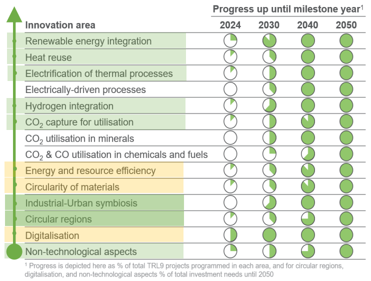
4 Transformation Levers
- Industrial-Urban Symbiosis
- Process Innovation
- Digitalisation
- Non-technological levers

16 Innovation Areas
Specifying what innovation is needed to meet the SPIRE ambitions

36 Innovation Programs
Specifying how SPIRE aims to achieve the required innovations

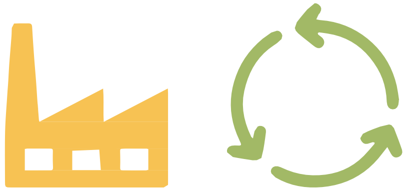
Processes4Planet Innovation to reach First deployment & deliver Impact

Unique cross-sectoral community



36 innovation programmes to FILL the GAP

+
Skills, Jobs,
Competitive gap analysis,
Framework/Standards



First-of-a-kind plants

Hubs for Circularity

Ambitions to enable Prosperity for all

0 Climate neutrality

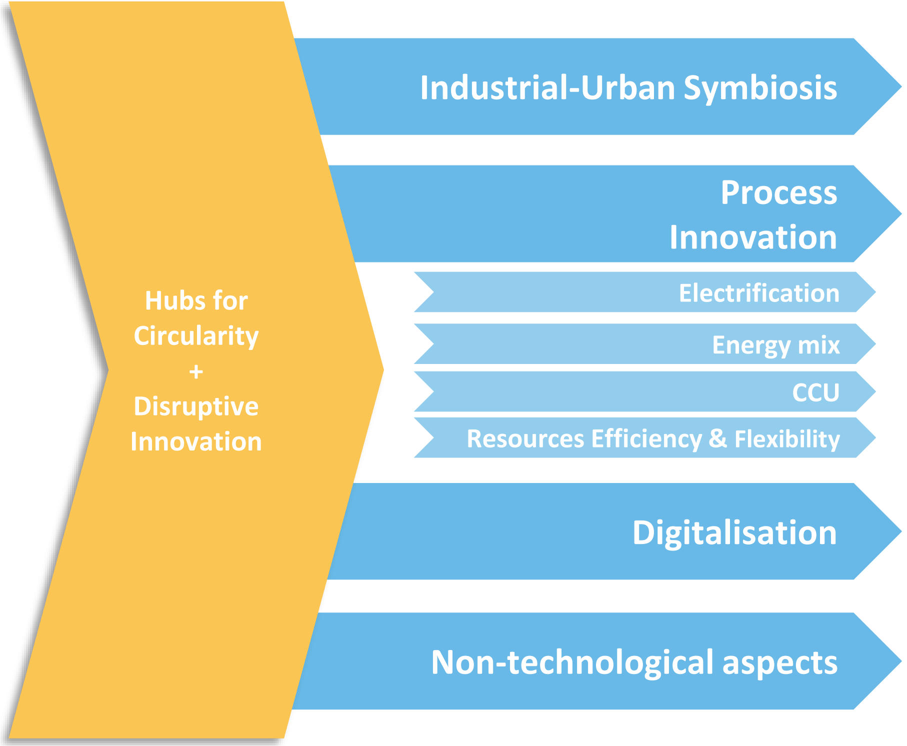
Near zero landfilling and near zero water discharge

Competitive EU process industries

Processes4Planet Innovation Areas progress towards 2050

Sustainable Process Industry through Resource and Energy Efficiency

Areas of common challenges



Progress up until milestone year[1]

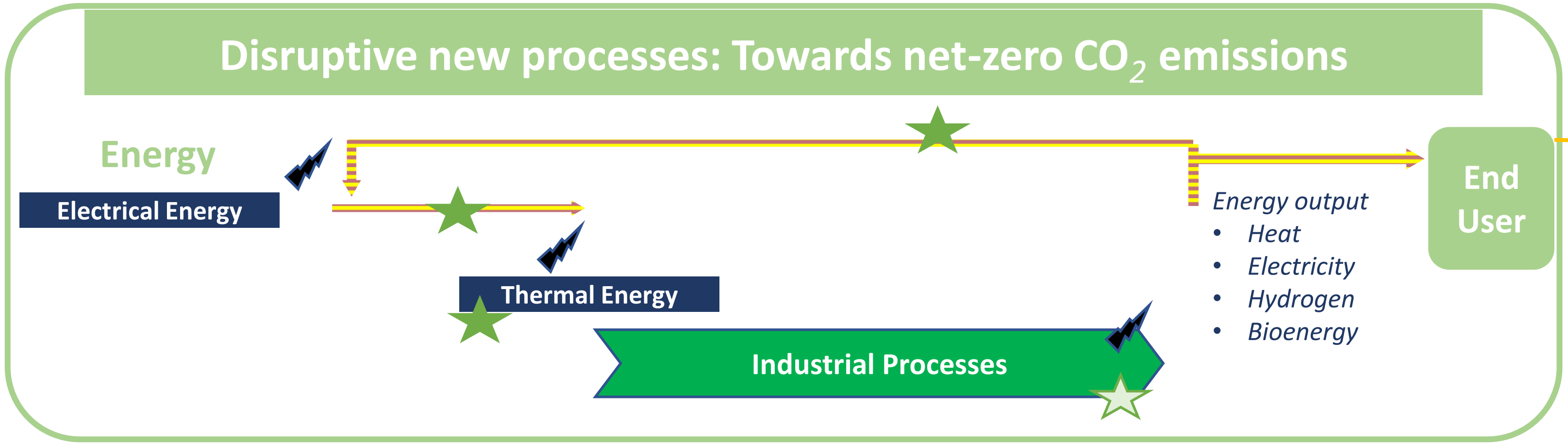
Innovation area	2024	2030	2040	2050
Renewable energy integration				
Heat reuse				
Electrification of thermal processes				
Electrically-driven processes				
Hydrogen integration				
CO_2 capture for utilisation				
CO_2 utilisation in minerals				
CO_2 & CO utilisation in chemicals and fuels				
Energy and resource efficiency				
Circularity of materials				
Industrial-Urban symbiosis				
Circular regions				
Digitalisation				
Non-technological aspects				

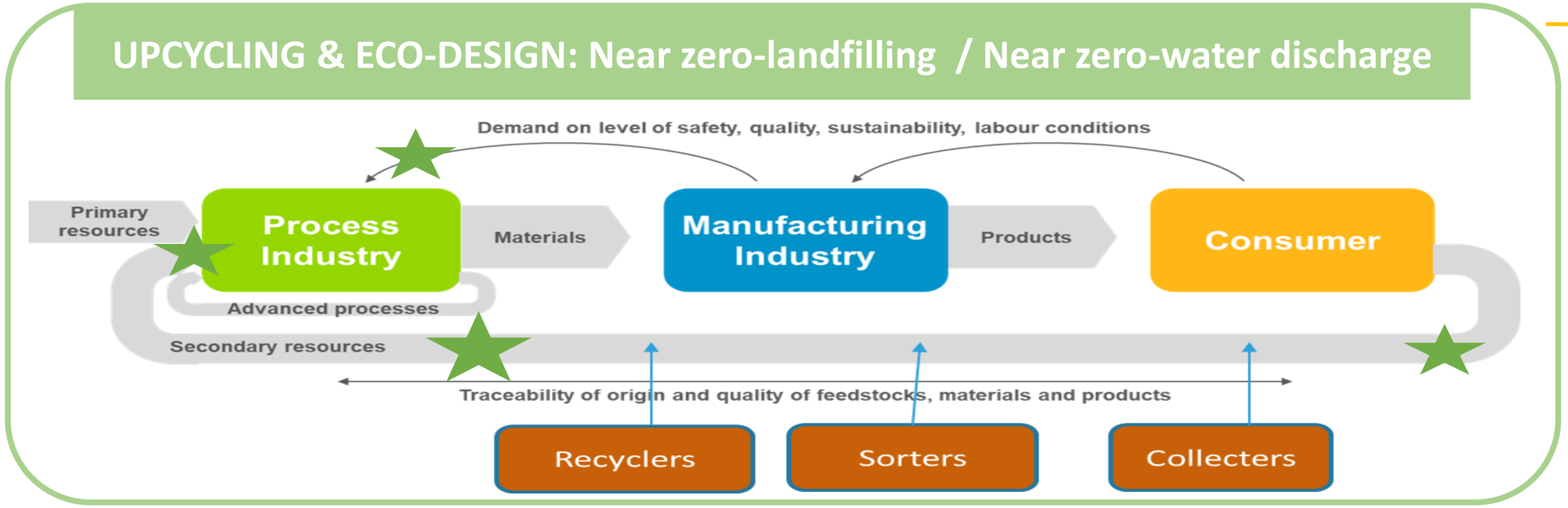
[1] Progress is depicted here as % of total TRL9 projects programmed in each area, and for circular regions, digitalisation, and non-technological aspects % of total investment needs until 2050

Combining efforts & ideas will accelerate innovations

Processes4Planet Innovation for Sustainable Prosperity

Sustainable Process Industry through Resource and Energy Efficiency



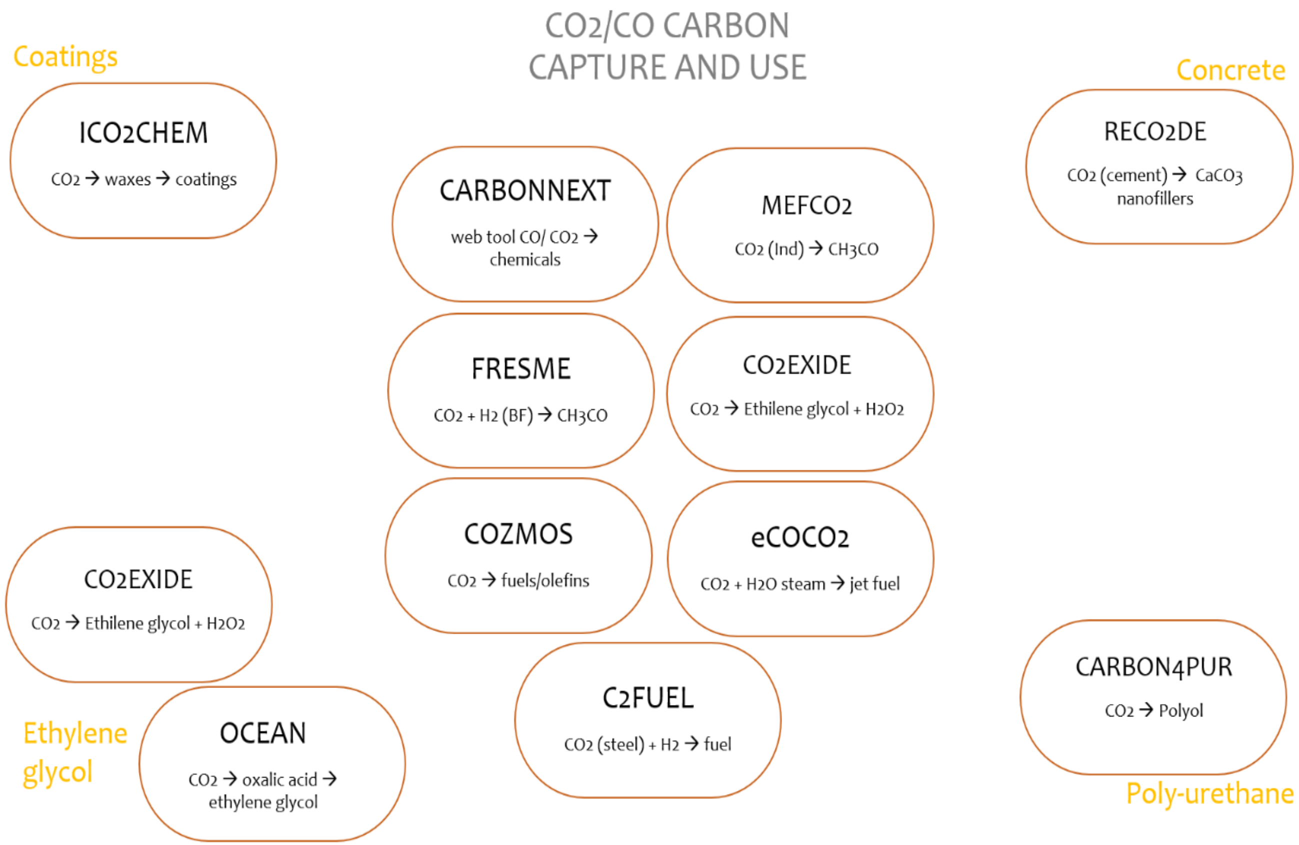


36 innovation programmes

SUCCESS STORIES PORTFOLIOS

Sustainable Process Industry through Resource and Energy Efficiency

CARBON CAPTURE AND USE STORIES



P4Planet *roadmap*

Building on the results of SPIRE projects

- **CLIMATE AMBITION:** towards the net-zero emissions scenario
- **Focus on:** process CO2 emissions and indirect emissions
- **Specific Objective 2:** Reduce emissions through CO/CO2 capture and use.
    - Develop new efficient CO/CO2 capture and purification technologies
    - Develop efficient CO2 valorisation routes to chemicals, minerals and fuels
- **KPI 2:** co2 eq. emissions reduction potential through CO2 Capture and Use measured through a relevant number of demonstrators. (Target: 100% reduction trajectory at TRL7)

CCU IN P4Planet roadmap

Sustainable Process Industry through Resource and Energy Efficiency

14 IAs	Innovation area	36 IPs	Innovation programme
1	Renewable energy integration	1a	Integration of renewable heat and electricity
		1b	Integration of bioenergy, waste and other new fuels
		1c	Hybrid fuel transition technologies
		1d	Flexibility and demand response
2	Heat reuse	2a	Advanced heat reuse
2	Electrification of thermal processes	3a	Heat pumps
		3b	Electricity-based heating technologies
4	Electrically-driven processes	4a	Electrochemical conversion
		4b	Electrically driven separation
4	Hydrogen integration	5a	Alternative hydrogen production routes
		5b	Using hydrogen in industrial processes
		5c	Hydrogen storage
6	**CO2 capture for utilisation**	6a	**Flexible CO2 capture and purification technologies**
7	**CO2 utilisation in minerals**	7a	**CO2 utilisation in concrete production**
		7b	**CO2 utilisation in building materials mineralisation**
8	**CO2 & CO utilisation in chemicals and fuels**	8a	**Artificial photosynthesis**
		8b	**Catalytic conversion of CO2 to chemicals or fuels**
		8c	**Utilisation of CO2 and CO as building block in polymers**
		8d	**Utilisation of CO to chemicals or fuels**
9	Energy and resource efficiency	9a	Next-gen catalysis
		9b	Breakthrough efficiency improvement
10	Circularity of materials	10a	Innovative materials of the process industries
		10b	Inherent recyclability of materials
		10c	Upgrading secondary resources
		10d	Wastewater valorisation
11	Industrial-Urban symbiosis	11a	Demonstration of Industrial-Urban Symbiosis
12	Circular regions	12a	European Community of Practice
		12b	Development of Hubs for Circularity
13	Digitalisation	13a	Digital materials design
		13b	Digital process development and engineering
		13c	Digital plant operation
		13d	Intelligent material and equipment monitoring
		13e	Autonomous integrated supply chain management
		13f	Digitalisation of industrial-urban symbiosis
14	Non-technological aspects	14a	Integration of non-technological aspects in calls
		14b	Human resources, skills and labour market

Processes4Planet Innovation for Sustainable Prosperity

Sustainable Process Industry through Resource and Energy Efficiency

UNLOCKING PRIVATE INVESTMENTS & BARRIERS TO MARKET FOR CLIMATE NEUTRAL & CIRCULAR SOLUTIONS

De-risk investments

Financial Flow up to TRL9

Define framework conditions for market uptake

Available & affordable green energy as enabler

Holistic digital process innovation 4.0 as accelerator

Hubs for Circularity to accelerate innovation

P4PLANET

Competitive Process Industry

Jobs

Skilled workforce

Sustainable Processes

Sustainable Materials

Shift to a real circular economy

Circular Regions

Export innovations worldwide (CO2 has no borders)

36 innovation programmes

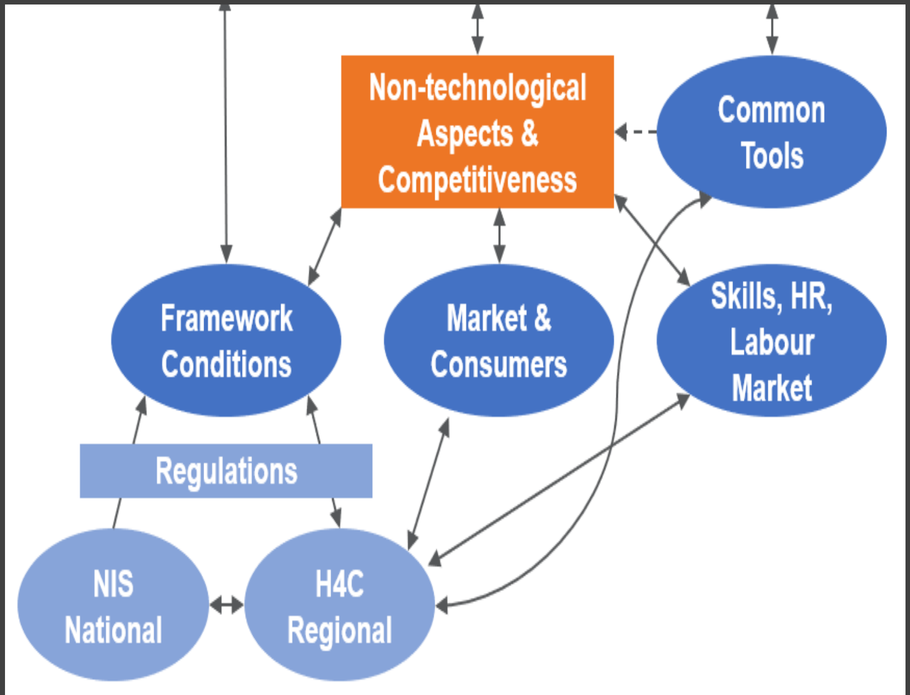
“European Energy Intensive Industry Skills Agenda and Strategy”
Erasmus+ Project

SPIRE/P4PLANET sectors and innovation eco-system working together for the skills of the future on Industrial-Urban Symbiosis and the Process Industry 4.0

Processes4Planet

NON-TECH & SOCIAL INNOVATION

Delivering more societal, economic and market impact.

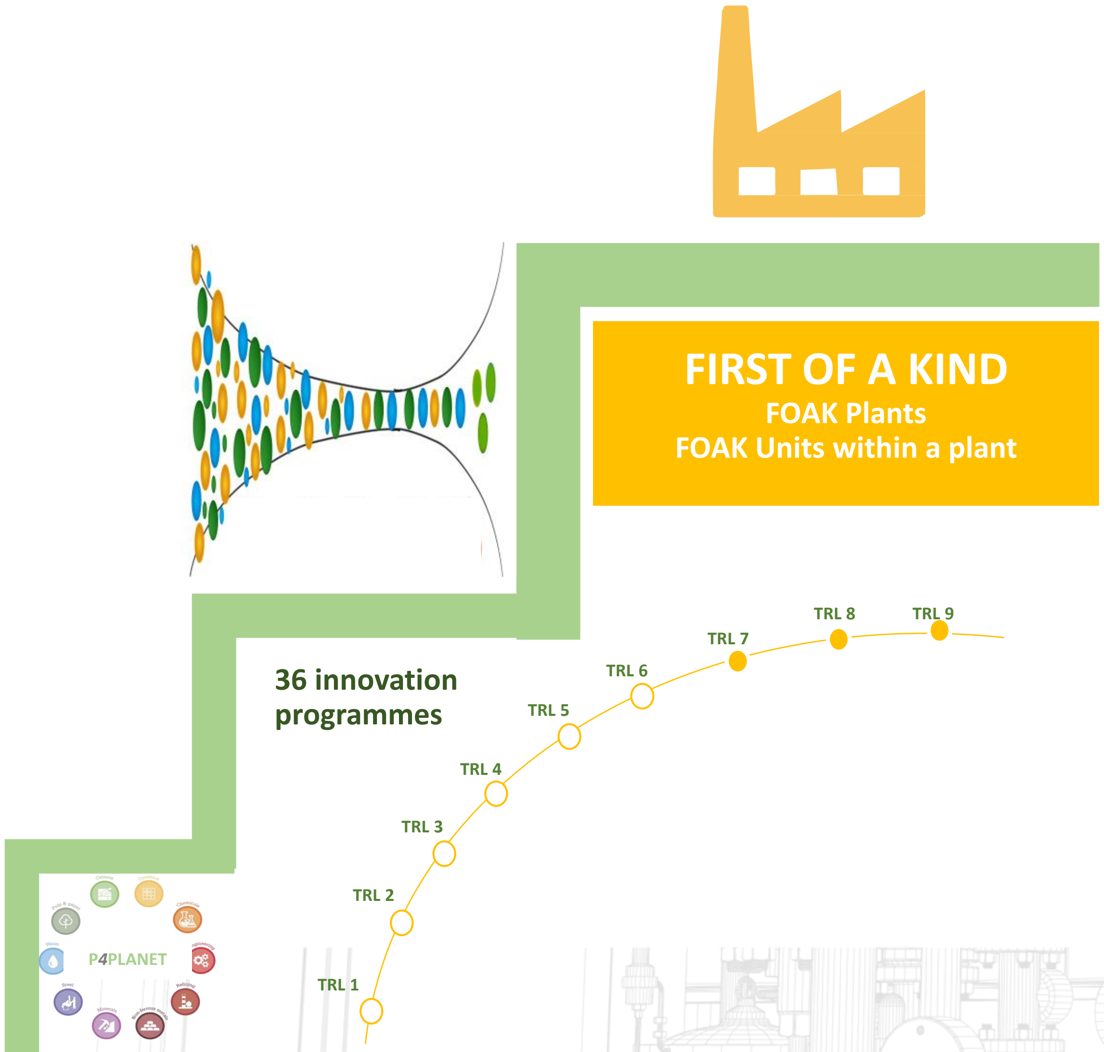


- EU, national & regional framework conditions
- Management of market & consumer demands & changes
- Effective common tools: LCA, business models, digital methodologies…
- Gender balance
- Human Resources, skills and labour market

Processes4Planet Objective: Impact

SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

MARBLES: a showcase of the Process Industry transformation

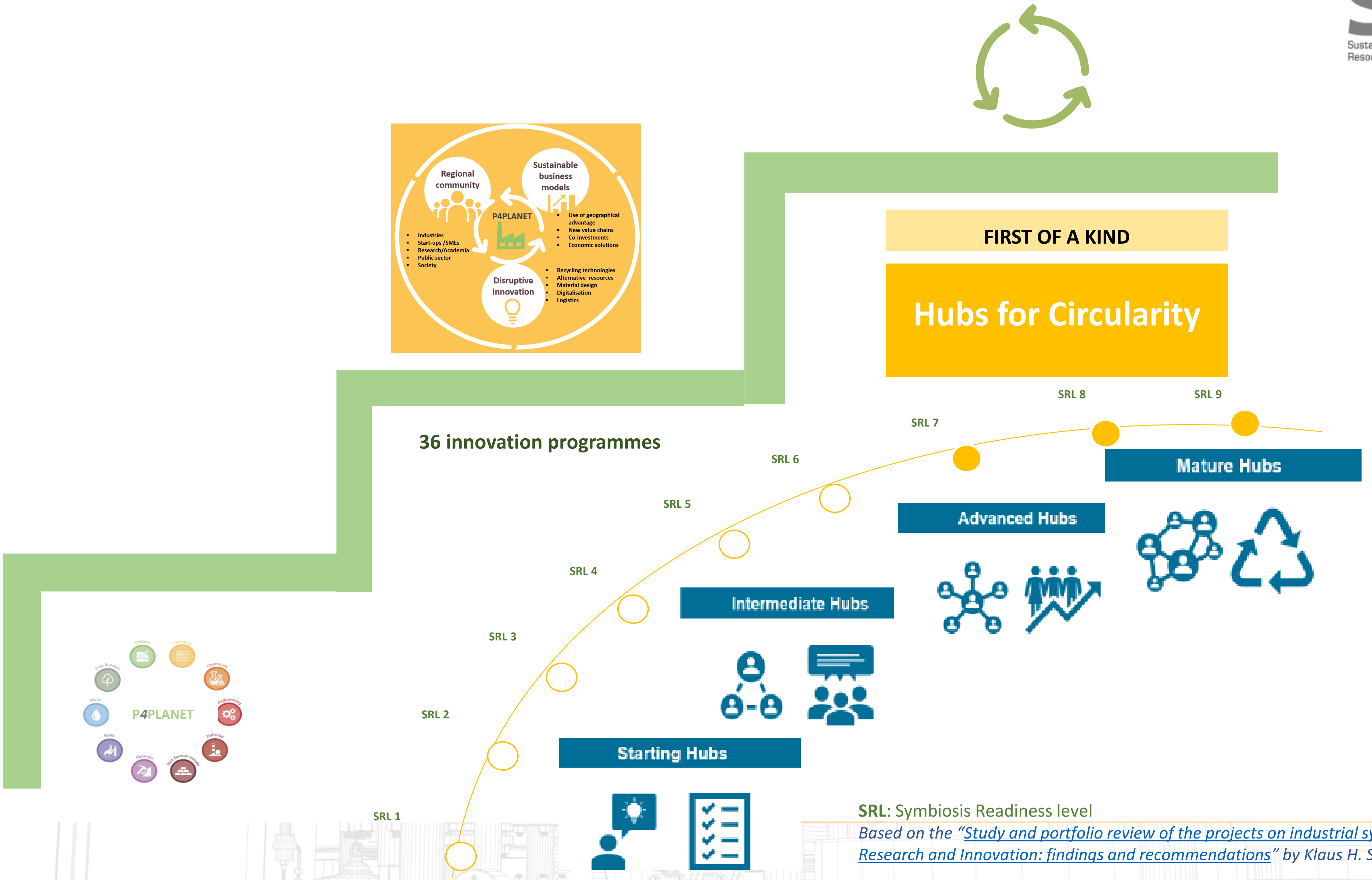


- **First-of-a-kind Large scale plants in operation**
- Combine one or several P4Planet Innovations towards the 2030/2050 ambitions to reach Climate neutrality and circularity
- Acting as Hubs of bulk amounts of resources from industry and the municipalities.
- Several marbles will likely connect to reach together the targets of the partnership's KPIs
- **50+ Marbles** identified of which ca. We aim to **launch 15 in the period 2021 – 2030**, responding to the green-deal plan, and enabled by the P4planet innovation portfolio

PRIVATE INVESTMENTS

- **Industry leader commitment**
- **when technical and economic feasibility is proved through Horizon Europe programs.**
- **Public support needed to de-risk and accelerate**

Processes4Planet HUBS FOR CIRCULARITY (2)



SRL: Symbiosis Readiness level

Based on the "Study and portfolio review of the projects on industrial symbiosis in DG Research and Innovation: findings and recommendations" by Klaus H. Sommer

Processes4Planet HUBS FOR CIRCULARITY (1)

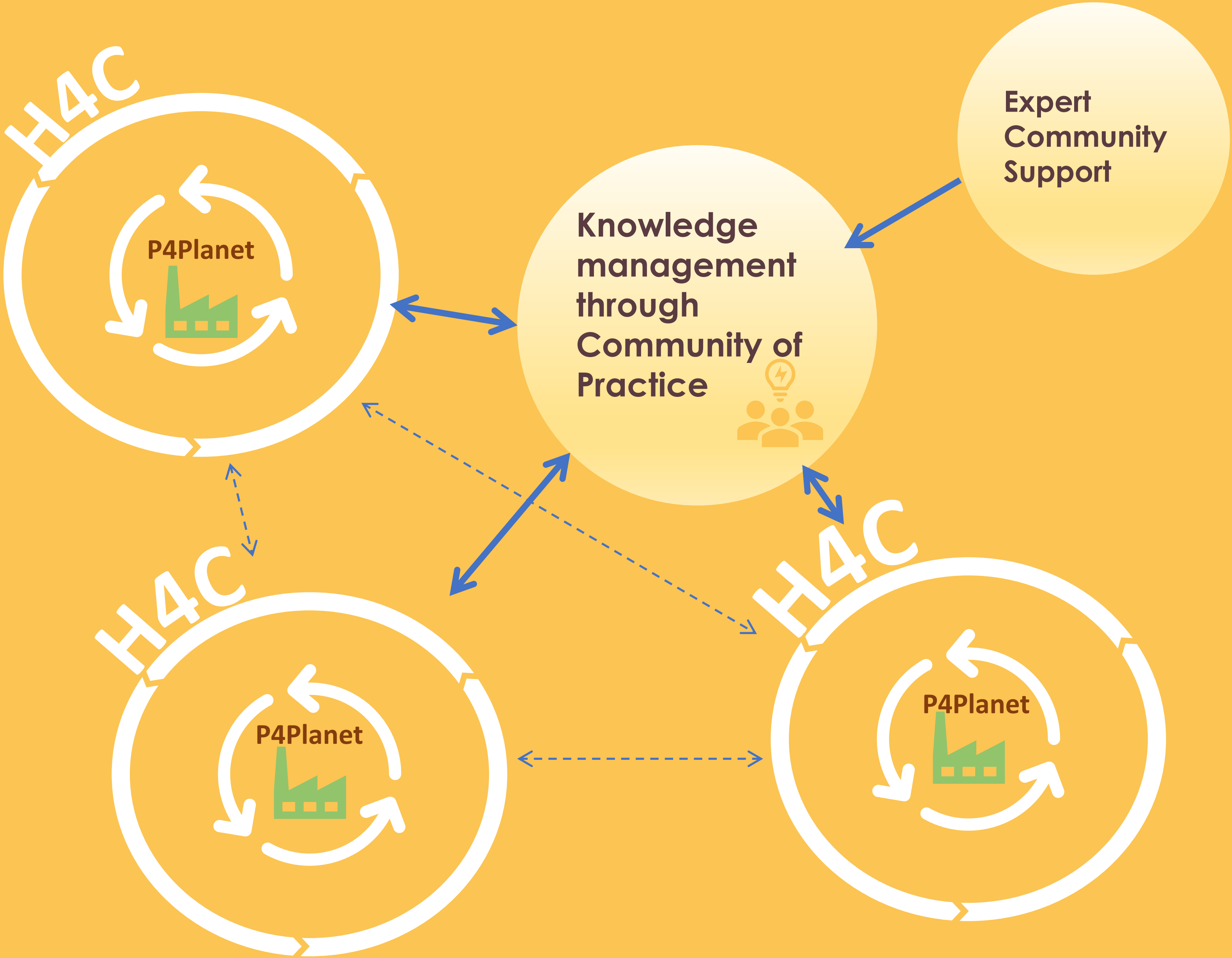
Systemic geographical proximity connected across EU regions

THE H4Cs CONCEPT

*Self-sustaining economic industrial ecosystems for **full-scale Industrial-Urban Symbiosis and Circular Economy, closing energy, resource and data loops** and bringing together all relevant stakeholders, technologies, infrastructures, tools and instruments necessary for their incubation, implementation, evolution and management.*

- → Territorial systemic solutions (regional approach)
- → **Processes4Planet inside!**
- → Facilitation necessary to overcome non-technological barriers to symbiosis

European Community of Practice



Platform for non-competitive exchange of **knowledge** and best practices

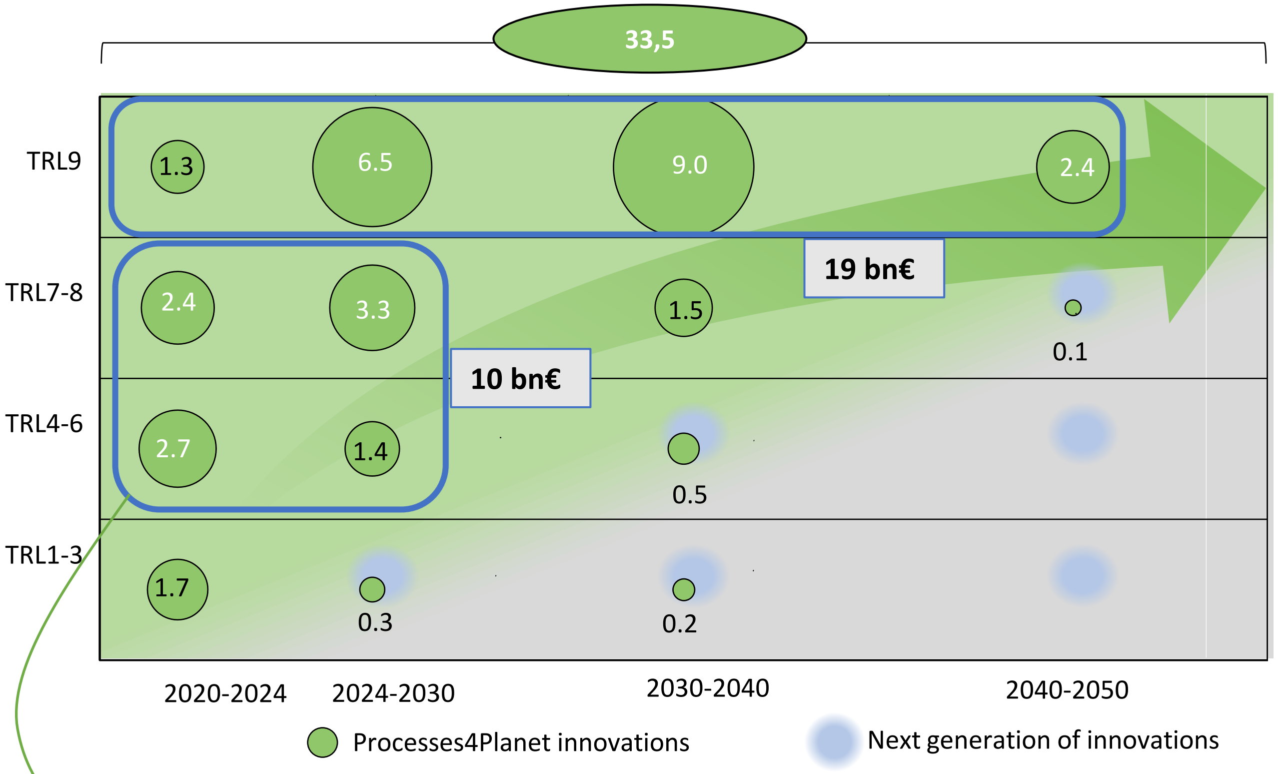
- Practical **toolbox**: technologies and tools
- **Innovation** programmes for finding the missing pieces in the puzzle of symbiosis
- **Modelling** circular concepts and plants of the future
- Enhancing **replicability**
- Communication and **transfer of technologies and solutions**
- Education and training
- **Sustainability** of the network

MASSIVE INVESTMENTS NEEDED TO REACH IMPACT

JOINING FORCES WILL HELP

Sustainable Process Industry through Resource and Energy Efficiency

R&I Investment needs (TRL 1- 9), € billion



Roll out investments

- Estimated in trillions €
- Two rounds of investments for PI before 2050

2050 impacts

Climate neutrality

Near zero landfilling and near zero water discharge

Competitive EU process industries

R&I Investments can be optimized if we avoid redundancies

WHY JOIN A.SPIRE

Teaming up to address the challenges of Climate Change, Circular Economy and Competitiveness together

LARGER INDUSTRIES:

- Continuous dialogue on R&I across SPIRE sectors and beyond
- Channel to raise your voice on R&I for HEU & other programmes
- Access to a pool of knowledge & talent (in Universities, research centres….)
- Direct access to SME providers
- Collaboration with the innovation ecosystem and value chain
- Access to developments by other projects, SMEs, universities…
- Protection of intellectual property
- Dialogue with the EC, MS, regions, MePs & other stakeholders

Further benefits to other members

SMEs:

- Direct Access to growth opportunities
- Direct Access to new markets
- Direct Access to large industry customers

RTOs, NGOs Innovation agencies et al.:

- Direct Access to applied innovation
- Link to deliver impact to society and regions
- Collaboration for disruptive innovations

SMEs in SPIRE: A Success Story

Growing above the EU-28 average

- 7 new employees / SME (higher than EU average = 2)
- 40% growth in turnover (+double than EU average)
- 27% of SMEs won new business through SPIRE contacts

Key to Process Innovation

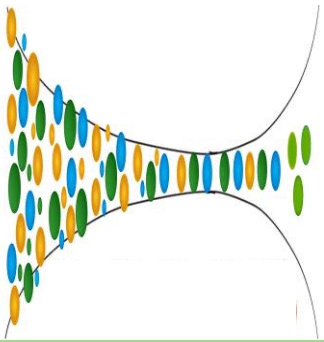
- Innovative SMEs delivering innovations for the Process Industry
- They develop the solutions with their customers
- The roadmap signals their market opportunities

SMEs ARE PARTNERS IN +100 SPIRE PROJECTS like Dryficiency, Dream, Reslag, Liberate, etc…
SMEs COORDINATE + 17 SPIRE ROJECTS like Scaler, Sharebox, Maestri, IdB, Spring, MultiCycle, etc…

Ceramics awarded as the most successful small sector in SPIRE projects

SMEs in P4PLANET: Key players & opportunities

Sustainable Process Industry through Resource and Energy Efficiency



First-of-a-kind plants

Hubs for Circularity

36 innovation programmes to FILL the GAP

SPECIALISED ON DIFFERENT AREAS:

- Process Innovation for the Process Industry
- Engineering
- IT
- Waste Management
- I-U Symbiosis
- Etc.

KEY PARTNERS IN P4PLANET PROJECTS

RAISE THE SMEs VOICE

- In Working Groups
- In the Advisory Group
- In the Board

Key players in the HUBS4CIRCULARITY

WHAT'S NEXT

- **February –March 2021:**
  - A.SPIRE members finalise topics and negotiations for P4Planet's MoU
  - Define new working structure within A.SPIRE
  - 8 to 17 Feb: **P4PLANET's ideation/brokerage event**
  - March (tbc): **follow up P4Planet's Brokerage event**
  - 19 March (A.SPIRE BoD) + 31st March (A.SPIRE General Assembly)
- **April 2021:** **Signature of Processes4Planet MoU with the European Commission**
- **May 2021:** **Processes4Planet launch event (Process Industry conference)**
- **April – June 2021**:
  - Kick-off of new working structure of A.SPIRE: engagement of our members
  - Kick-off of the new governance and advisory structures of Processes4Planet: Partnership Board, Feedback Panel and Impact Panel
  - 19 June: A.SPIRE BoD meeting
- **September - November 2021:** **Projects & H4Cs Forum** + Board meeting

Connected across borders and to citizens

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Rue Belliard 40, Bte 21
1140 Brussels

Session 2A (chairperson Giampaolo Manzolini)	
15:00-15:20	Dr. G. Garcia - LCA and TEA of the COZMOS technology
15:20-15:40	Dr. A. Mattos or Dr. A. Mitchell - How can public policy and business model innovation be developed to address challenges of CCUS and realise the opportunity?
15:40-16:00	Dr. L. Engelmann - Perception of CO_2-based fuels and their production in international comparison
16:00-16:20	Dr. N. Dunphy - Social studies in REALISE project

ORGANIZED BY

SPONSORED BY

LCA and TEA of the COZMOS technology

Guillermo Garcia-Garcia
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UK Centre for Carbon Dioxide Utilisation
The University of Sheffield

International Workshop on CO2 Capture and Utilization
16-17 February 2021

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

Contents

- Introduction to LCA and TEA methodologies
- Literature review of LCA studies of CCU products
- Environmental analysis of catalysts
- Initial stages of the full LCA and TEA for COZMOS
- Conclusions

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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CO2MOS

LCA and TEA methodologies

- As research in CCU matures, investors and funders require clarification on the credentials of these technologies
- Governments and regional authorities are creating roadmaps and require clarity on CCU options
- Companies are trying to choose between bio-based, CCU and other waste routes to create their products and need data for comparisons
- Life-Cycle Assessment (LCA) can help us to analyse environmental consequences of decisions
- Techno-Economic Assessment (TEA) can help us to analyse economic consequences of decisions
- Both LCA and TEA allow technologies to be compared

What are the environmental and economic consequences of CCU?

Can CCU reduce CO_2 emissions and be economically profitable?

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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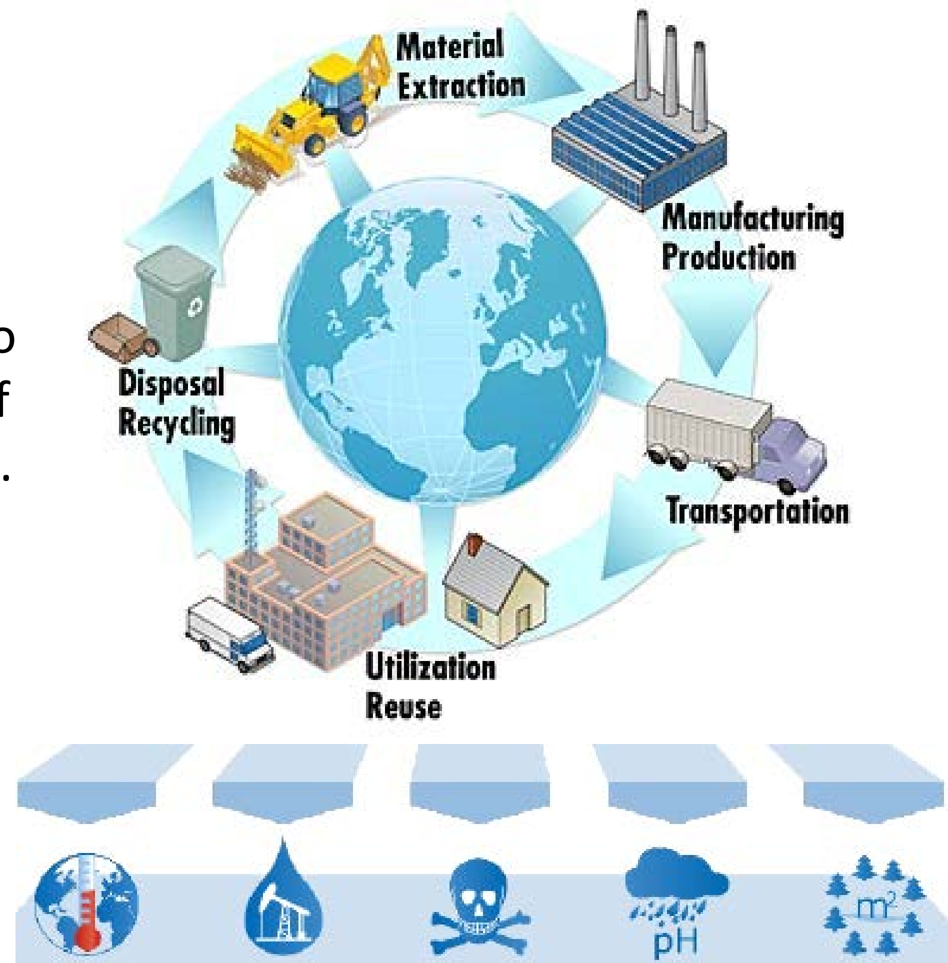
Definition of LCA

Life-cycle assessment is a methodology to account for the environmental impacts of a product, service, process, company, etc. throughout its entire life cycle



COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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Structure of LCA studies

INTERNATIONAL STANDARD **ISO 14040**

Second edition
2006-07-01

Environmental management — Life cycle assessment — Principles and framework

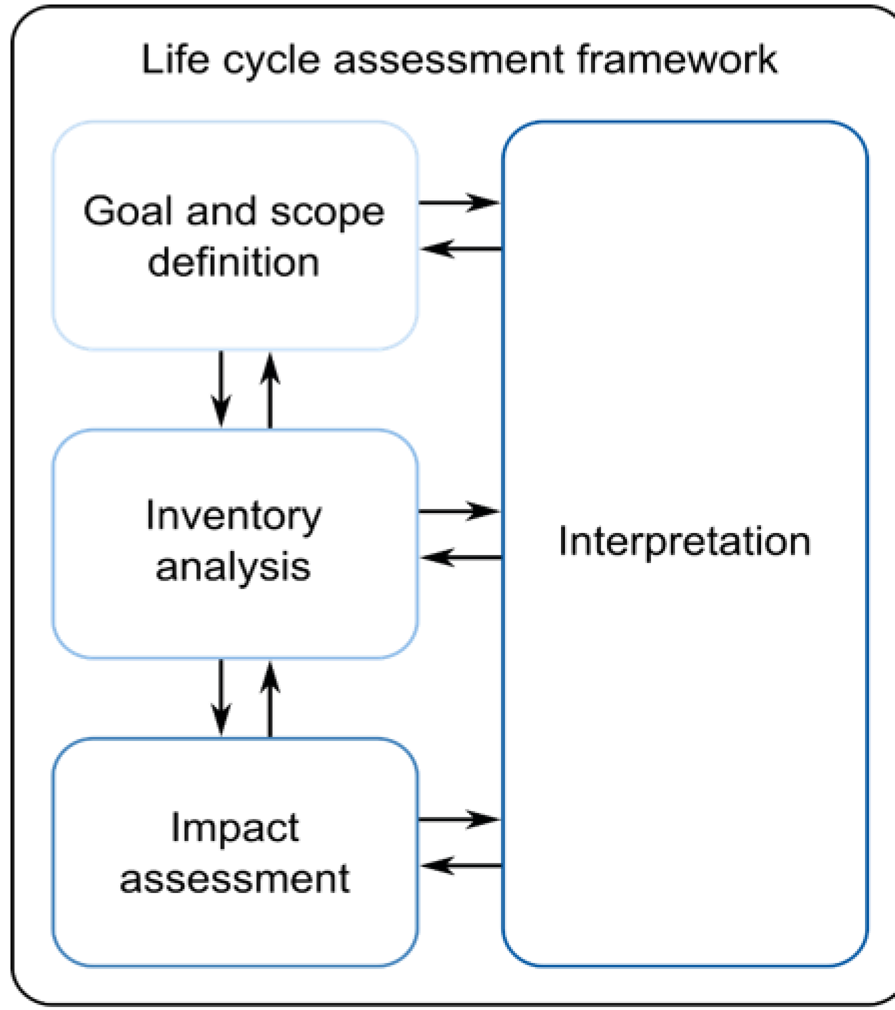
Management environnemental — Analyse du cycle de vie — Principes et cadre

INTERNATIONAL STANDARD **ISO 14044**

First edition
2006-07-01

Environmental management — Life cycle assessment — Requirements and guidelines

Management environnemental — Analyse du cycle de vie — Exigences et lignes directrices



2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
pean Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

Literature review

- Following CCU products studied:
  methanol, methane, DME, DMC, propane and propene

1. Formulation of review questions → 2. Definition of a precise review scope → 3. Location of literature → 4. Selection and evaluation of relevant literature → 5. Literature analysis → 6. Reporting of the findings

Methodology for analytical review

Research questions

1. What are the most promising products that could be produced from CO_2?
2. What are the potential environmental impacts and/or benefits of producing these products from CO_2, in comparison with traditional methods?
3. What is the level of application of the LCA methodology to study CCU?

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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Literature review – general findings

- Large potential from CCU for a number of feedstocks
- Main constraints:
  - Availability of green hydrogen. If hydrogen is from fossil sources or current grid mix, the environmental benefits can be reduced or disappear
  - The origin of electricity has a key role in determining the final environmental impact of the process. Current grid mix is unfavourable, future scenarios need to be realistic
  - CO_2 capture, separation, purification and transport needs have a high impact
- Need for full LCAs to assess the environmental impacts
  - Not only look at Global Warming Potential or carbon footprint, but also other impacts
  - All life cycle stages have to be considered for a consistent, robust analysis
- A strong value chain is required to support the production of CO_2-based products

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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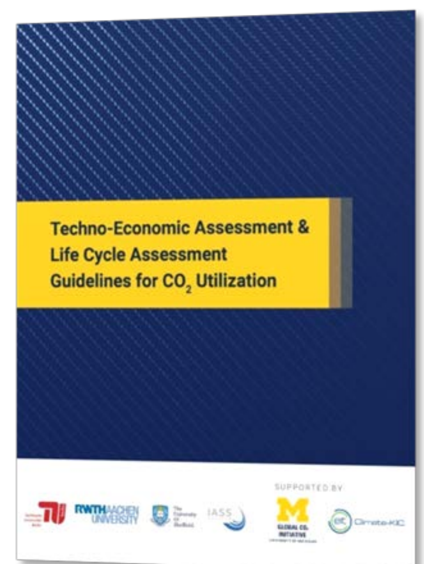
Literature review – use of LCA to analyze environmental impacts of CCU technologies

- Few LCA studies of CCU systems have been undertaken so far
- Often, significantly different results are obtained for LCA studies carried out for the same CO_2-based product manufactured by the same route
- Main reasons behind this are different assumptions about the supply of feedstocks (e.g. CO_2, H_2 and electricity), definition of the system boundaries, and the way to allocate products and co-products (i.e. multi-functionality issues)
- Most studies focus on climate change or global warming only, omitting the rest of the environmental impact categories
- A common framework for LCA of CCU is needed: in addition to generic LCA standards (e.g. ISO 14040, ILCD Handbook) we are using The Guidelines for LCA and TEA of CCU



COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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More information in our journal article

- "Analytical review of Life Cycle Environmental Impacts of Carbon Capture and Utilization Technologies"

- Published in ChemSusChem in January 2021

- Open Access, free to download at:

https://chemistry-europe.onlinelibrary.wiley.com/doi/abs/10.1002/cssc.202002126

doi: 10.1002/cssc.202002126

Analytical Review of Life-Cycle Environmental Impacts of Carbon Capture and Utilization Technologies

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Abstract

Carbon capture and utilization (CCU) has been proposed as a sustainable alternative to produce valuable chemicals by reducing the global warming impact and depletion of fossil resources. To guarantee that CCU processes have environmental advantages over conventional production processes, thorough and systematic environmental impact analyses must be performed. Life-Cycle Assessment (LCA) is a robust methodology that can be used to fulfil this aim. In this context, this article aims to review the life-cycle environmental impacts of several CCU processes, focusing on the production of methanol, methane, dimethyl ether, dimethyl carbonate, propane and propene. A systematic literature review is used to collect relevant published evidence of the environmental impacts and potential benefits. An analysis of such information shows that CCU generally provides a reduction of environmental impacts, notably global warming/climate change, compared to conventional manufacturing processes of the same product. To achieve such environmental improvements, renewable energy must be used, particularly to produce hydrogen from water electrolysis. Importantly, we identified different methodological choices being used in the LCA studies, making results not comparable. There is a clear need to harmonize LCA methods for the analyses of CCU systems, and more importantly, to document and justify such methodological choices in the LCA report.

Keywords

Carbon capture and utilization • environmental analysis • life-cycle analysis • sustainable chemistry • renewable resources

1 Introduction

Global anthropogenic fossil CO_2 emissions have continuously increased over the last decades, peaking at 37.9 Gt in 2018 [1]. They represent over 75% of the total anthropogenic greenhouse gas (GHG) emissions [1], causing global warming and therefore affecting the Earth's climate system. IPCC [2] estimates that, if these emissions keep growing at the current rate, global

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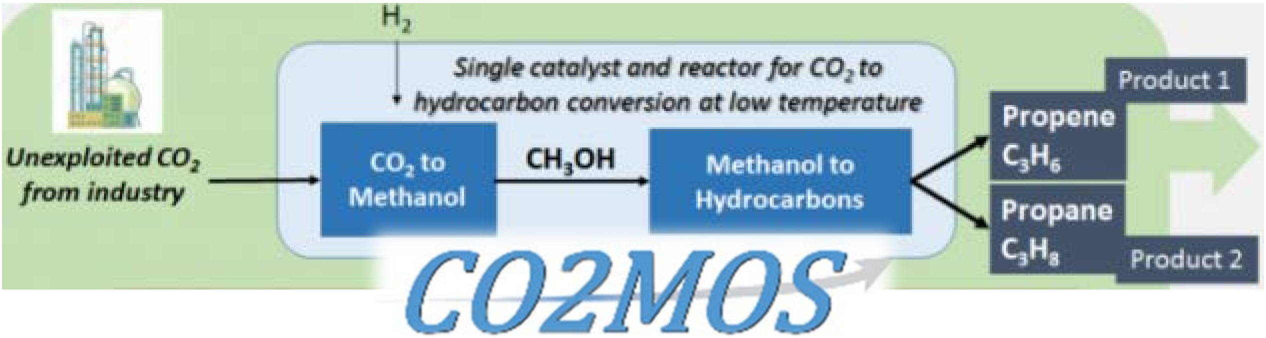
Environmental impacts of catalysts



- Catalyst compared:
  - ✓ $ZnO:ZrO_2$ / ZSM-5
  - ✓ $PdZn@ZrO_2$ / SAPO-34
  - ✓ $ZnCeZrO_x$ / H-RUB-13
- Cradle to gate comparison
- The comparison was initially done in terms of 1 g of catalyst produced

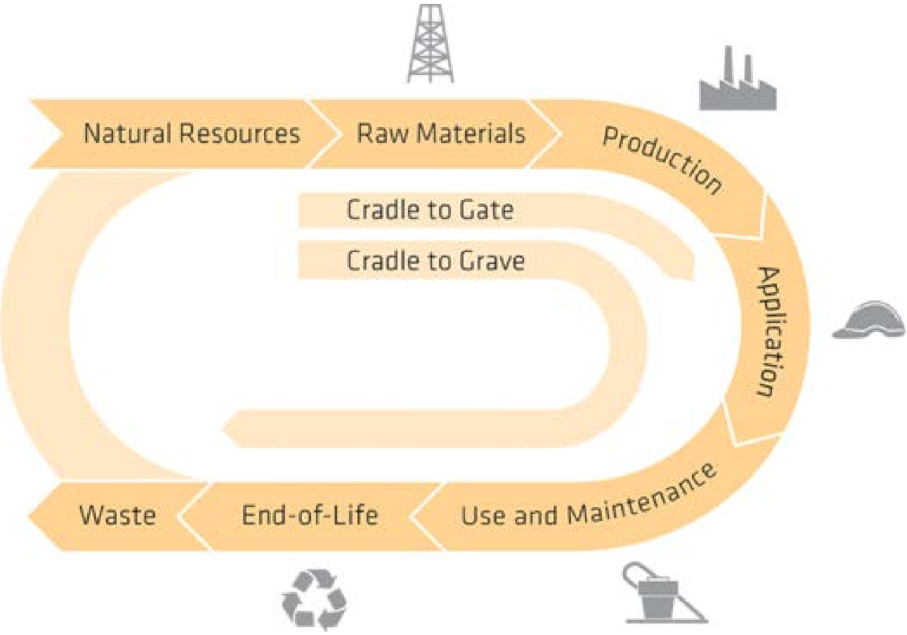


Diagram source: Silka Concrete

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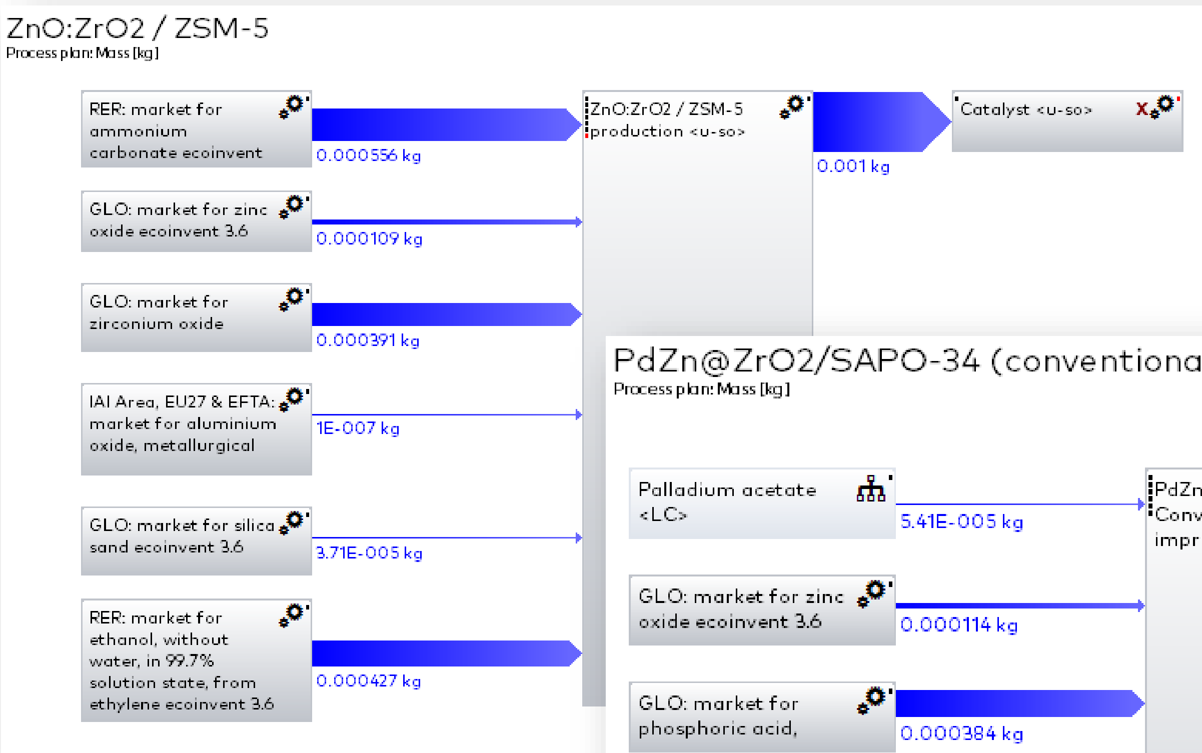
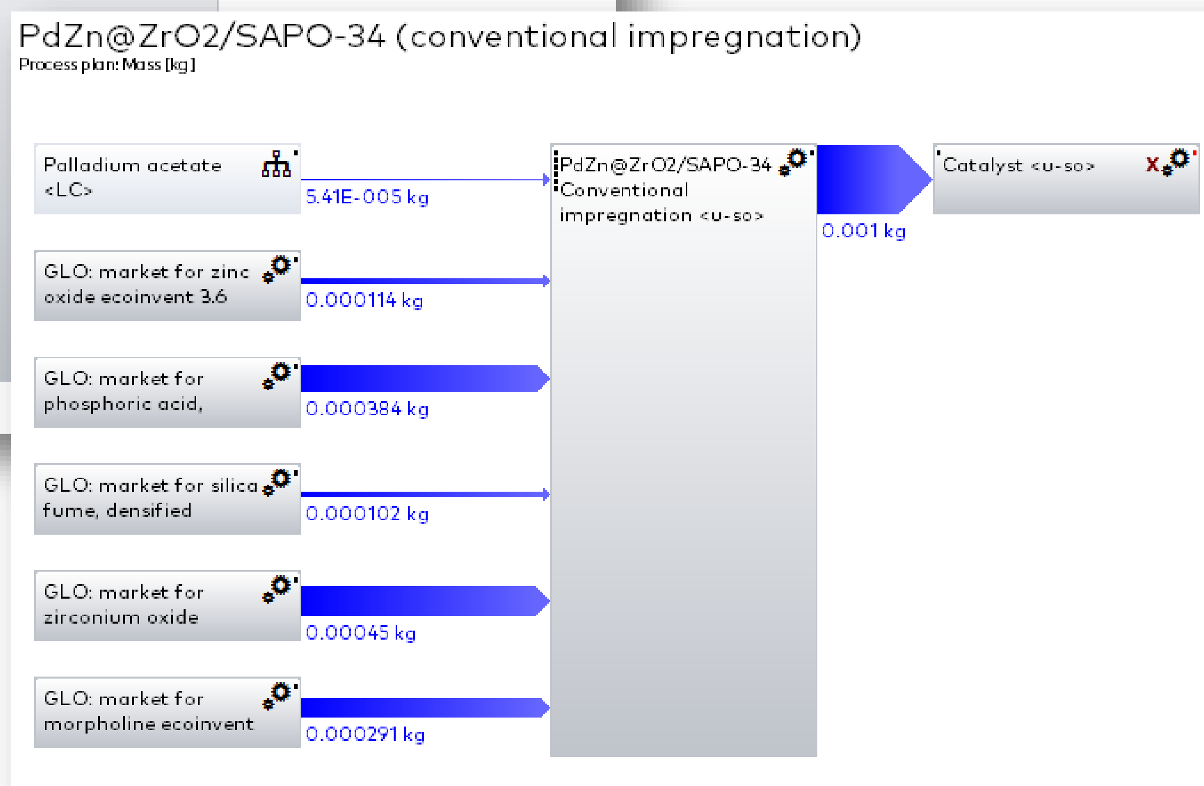
GaBi models



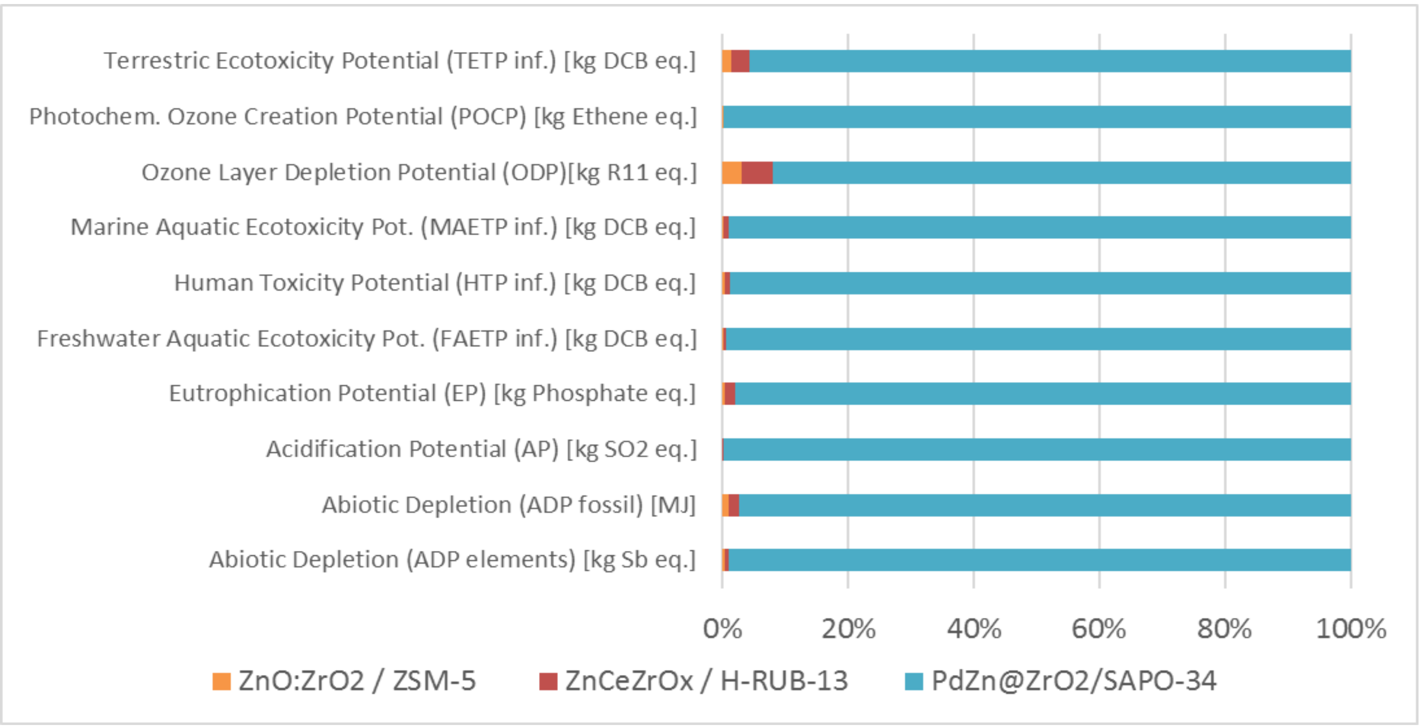
ZnO:ZrO2 / ZSM-5
Process plan: Mass [kg]
RER: market for ammonium carbonate ecoinvent
0.000556 kg
GLO: market for zinc oxide ecoinvent 3.6
0.000109 kg
GLO: market for zirconium oxide
0.000391 kg
IAI Area, EU27 & EFTA: market for aluminium oxide, metallurgical
1E-007 kg
GLO: market for silica sand ecoinvent 3.6
3.71E-005 kg
RER: market for ethanol, without water, in 99.7% solution state, from ethylene ecoinvent 3.6
0.000427 kg
ZnO:ZrO2 / ZSM-5 production <u-so>
0.001 kg
Catalyst <u-so>



PdZn@ZrO2/SAPO-34 (conventional impregnation)
Process plan: Mass [kg]
Palladium acetate <LC>
5.41E-005 kg
GLO: market for zinc oxide ecoinvent 3.6
0.000114 kg
GLO: market for phosphoric acid,
0.000384 kg
GLO: market for silica fume, densified
0.000102 kg
GLO: market for zirconium oxide
0.00045 kg
GLO: market for morpholine ecoinvent
0.000291 kg
PdZn@ZrO2/SAPO-34 Conventional impregnation <u-so>
0.001 kg
Catalyst <u-so>

Environmental impact results

- With the assumptions of the study, the catalyst with palladium had the largest global warming potential, most of it coming from the palladium content
- The catalyst with the lowest GWP is ZnO:ZrO2/ZSM-5



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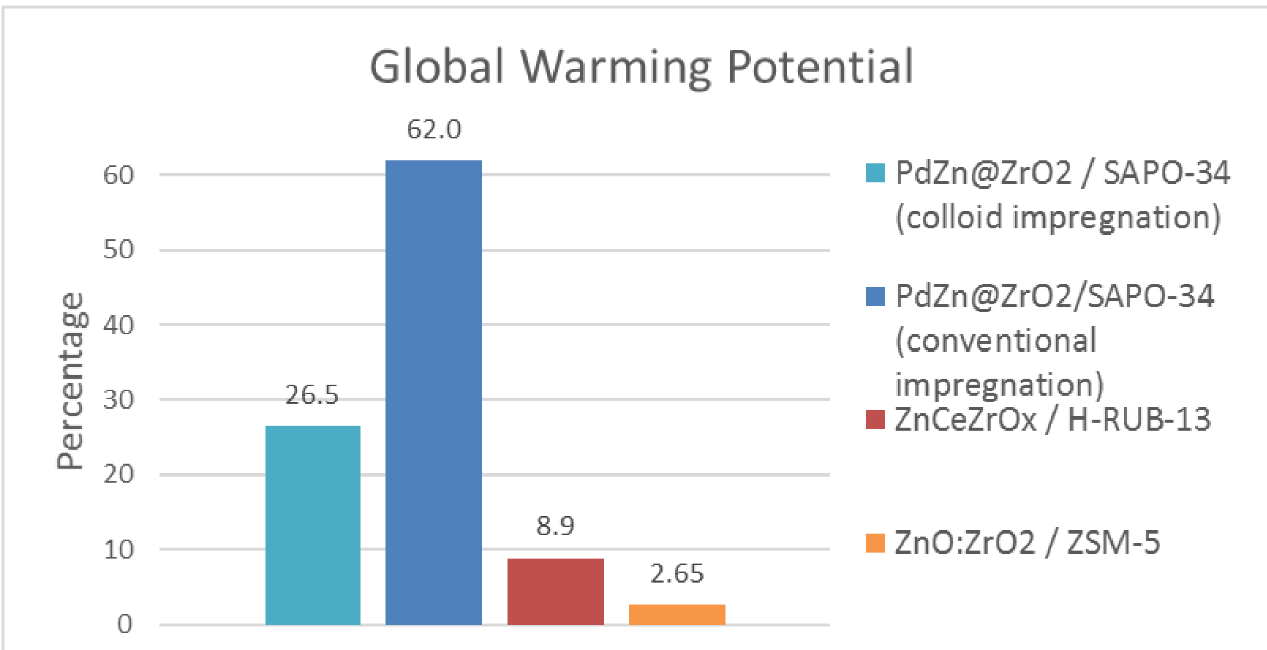
Sensitivity analysis

- We also did sensitivity analysis for the catalyst preparation method and the reaction yield
- Including the increased yield, reduced the relative impact of the catalyst compared to the other ones, but remained the highest one



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Definition of TEA

- Techno-Economic Assessment (TEA) is a **methodology to analyze the technical and economic** performance of a process, product or service
- TEA integrates **cost, revenue and technical criteria** with a general focus on the production phase (but not always) – typically gate to gate type studies
- TEA is an assessment methodology that can aid in making decisions
- TEA can be used to feed back recommendations during the design phase
- TEA results are specific to a scenario/context

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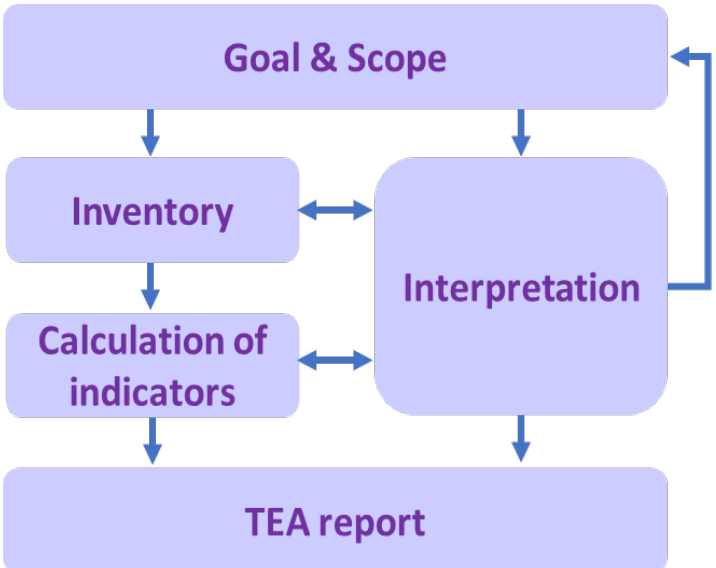
Structure of TEA studies



TEA is built on the framework outlined in the LCA ISO

- **Goal** provides guidance for the overall study
- **Scope** defines the system boundary
- **Inventory** collects the relevant data
- **Calculation** produces results
- **Interpretation** assesses the quality of results, provides recommendations & conclusions
- **Reporting** captures the outputs of the study in a form that can be communicated consistently and transparently

TEA is an iterative process – we often go back and make adjustments

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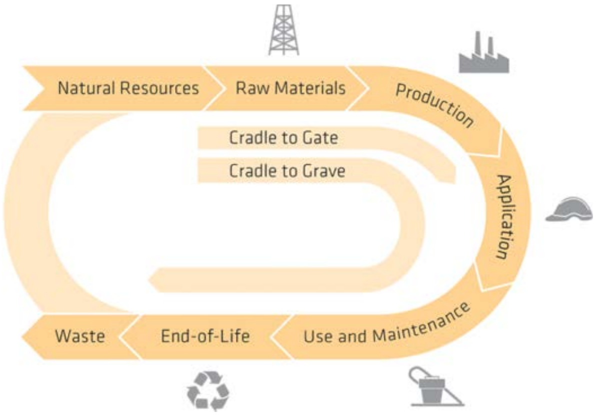
Scope of LCA and TEA studies

- Both **LCA** and **TEA** will be aligned
- **The main goal** is to assess whether the use of carbon intensive gases from the steel industry and the petrochemical refinery to produce propane and propene would have an economic and/or environmental benefit when compared to the conventional production of those products
- **Gate to gate** study

  Upstream operations are unchanged in the different scenarios so they are not included



- **Functional unit**:

  Production of 1 kg of propane

  All the products will be considered in the study even if they are not part of the functional unit

  The product distribution can be adjusted with the reactor conditions

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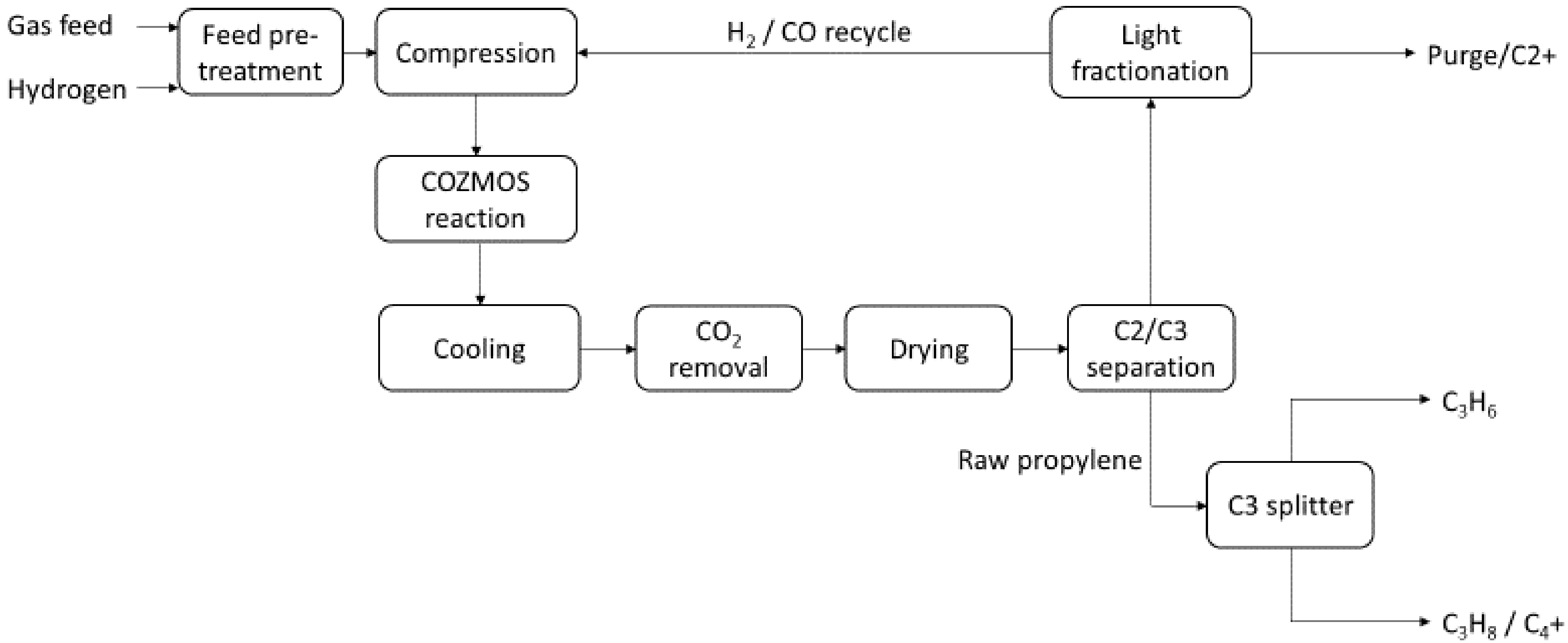
COZMOS process



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LCA and TEA scenarios

4 main scenarios considered:

1. Tata Steel reference or baseline case, where the BFG is sent offsite for electricity generation
2. Tata Steel COZMOS scenario, where BFG is used within COZMOS
3. Tupras reference case, where the PSA tail gas is used for heating
4. Tupras COZMOS scenario, where the PSA tail gas is used for the COZMOS process

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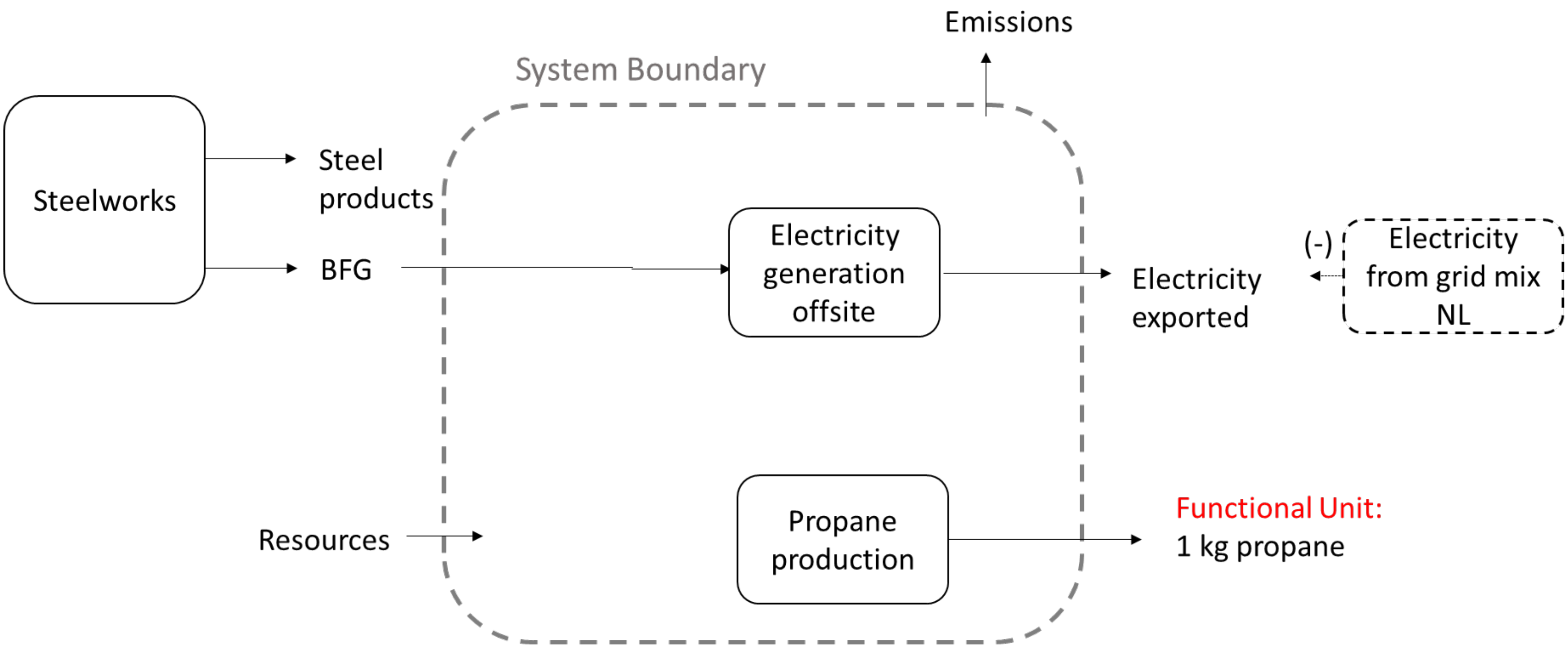
Scenario 1: Reference case, Tata Steel



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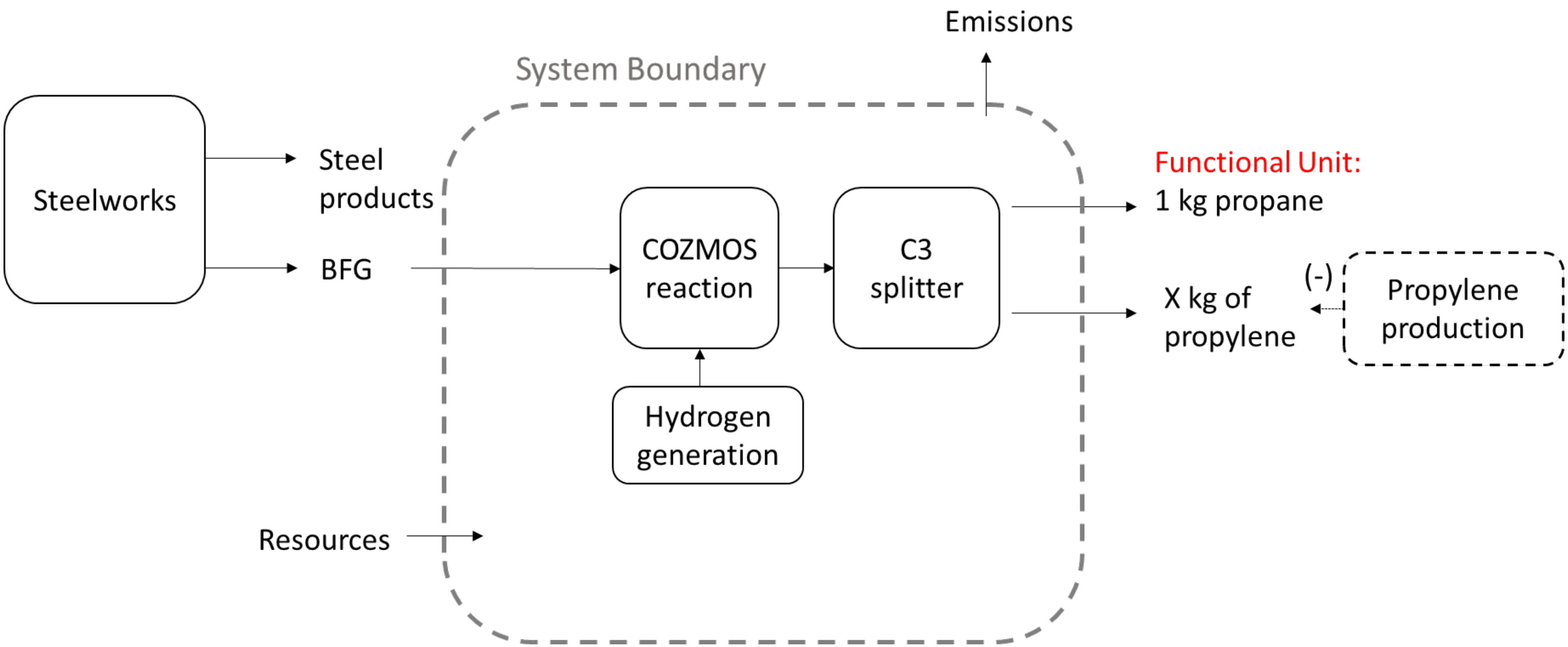
Scenario 2: COZMOS scenario, Tata Steel



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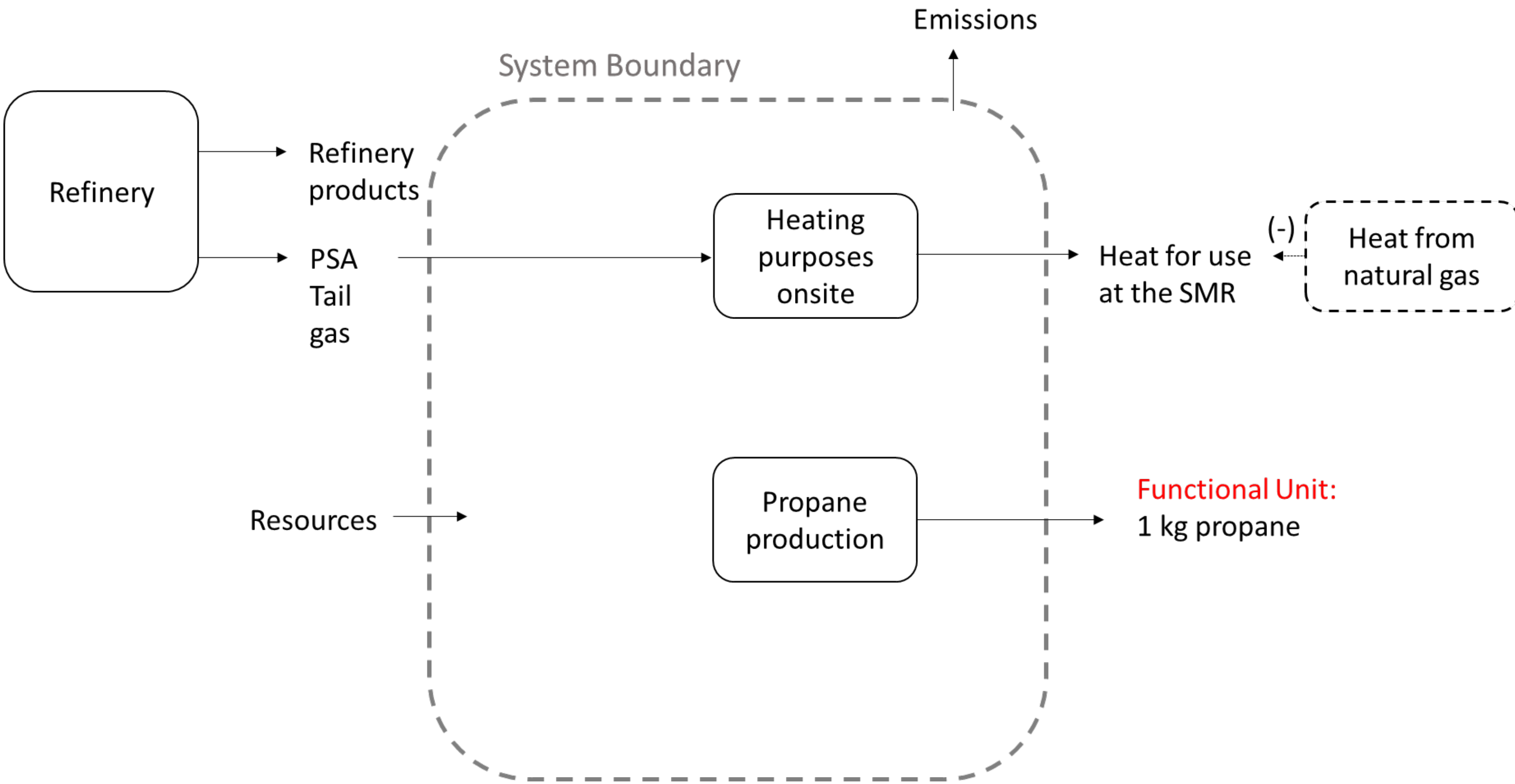
Scenario 3: Reference case, Tupras



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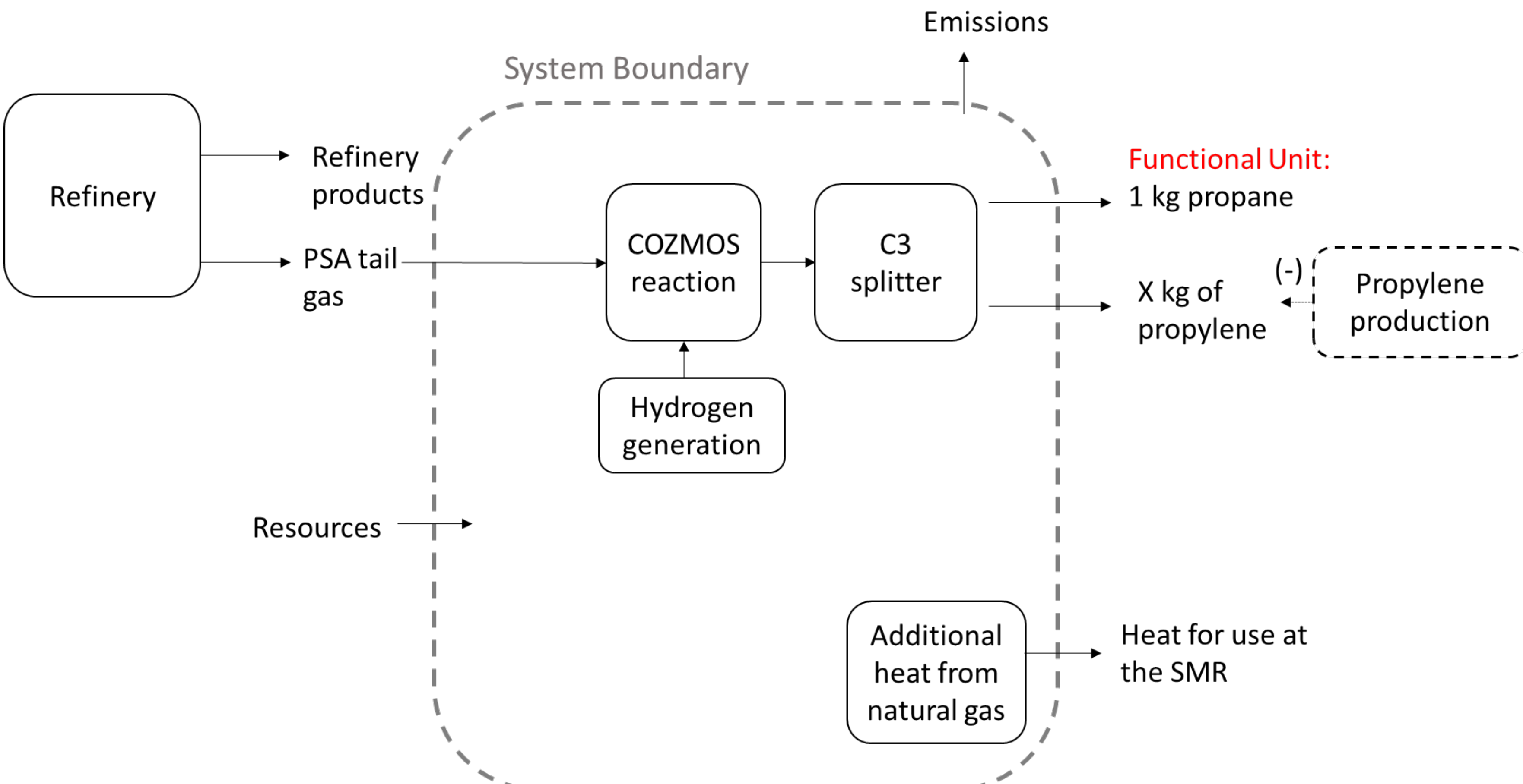
Scenario 4: COZMOS scenario, Tupras



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The Guidelines for LCA & TEA of CCU

Project goal:

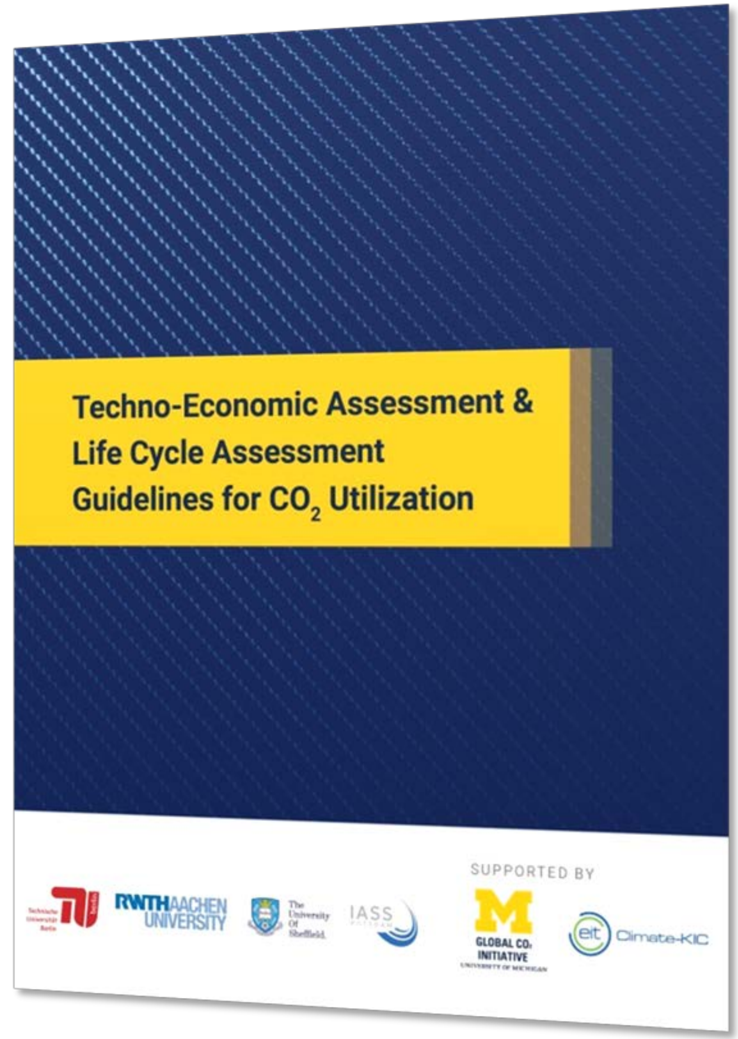
- Define a common assessment language to push R&D, investment and commercialization of CCU
- Align LCA and TEA
- Enhance transparency and comparability
- Enable strong acceptance and adoption of guidelines

Available at:

http://umlib.us/CO2Guidelines

DOI: 10.3998/2027.42/145436

ISBN: 978-1-916 4639-0-5



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Conclusions

- LCA allows you to calculate the environmental impacts throughout a product or process life time
- TEA allows you to analyze the technical and economic performance of a process or product
- LCA and TEA can support decisions based on environmental and techno-economic performance
- We are using LCA to identify possible bottlenecks in the process
- We applied a streamlined LCA to potential catalysts to rank them according to their environmental impact
- We are undertaking full LCA and TEA of the COZMOS process in accordance with existing standard references and guidelines

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The University Of Sheffield.

Marta Cruz Fernandez, Steven Woolass

Tata Steel

TATA STEEL

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Thank you for your attention

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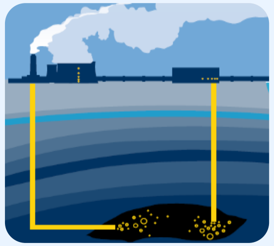



CCUS business models & public policy support

Addressing challenges and realizing opportunities for CCUS

C4U

February 2021

elementenergy

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Element Energy, a consultancy focused on the low carbon energy sector

Element Energy covers all major low carbon energy sectors:

CCUS & industrial decarbonisation

Energy Networks

Smart Energy Systems

Hydrogen

Low Carbon Transport

Built Environment

Selected clients:

Public sector

- Department for Business, Energy & Industrial Strategy
- Committee on Climate Change
- European Commission
- Transport for London
- Transport Scotland
- Birmingham City Council
- scottishcitiesalliance (Aberdeen • Dundee • Edinburgh • Glasgow • Inverness • Perth • Stirling)
- seai Sustainable Energy Authority of Ireland
- Greater London Authority

NGOs

- iea International Energy Agency
- European Climate Foundation
- UNDP
- World Bank Group

Public-Private Partnerships

- energy technologies institute
- UK H_2 Mobility
- LowCVP low carbon vehicle partnership
- FCH Fuel Cells and Hydrogen Joint Undertaking

Private Sector

- Shell
- OGCI Oil and Gas Climate Initiative
- Equinor
- bp
- Toyota
- Nissan
- UK Power Networks
- Hyundai
- EDF Energy
- Scottish and Southern Energy
- Air Products
- British Gas
- Bosch Invented for life
- Rolls-Royce
- ESB Energy for generations
- BOC Member of The Linde Group
- Nissan
- Daimler
- nationalgrid
- zipcar

Agenda

The C4U Project (H2020)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884418

C4U: Advanced Carbon Capture for Steel Industries Integrated in CCUS Clusters (Horizon 2020 Funded Project)

Testing and demonstration of capture technologies at TRL7
(WP1 & WP2)

Impact: Successful demonstration of CO2 capture from industrial sources

Integrating CO_2 capture in industrial installations and clusters
(WP3 & WP4)

Impact: Economic and safe demonstration of integrated CCUS value chain

Societal readiness, public policy and the business case
(WP5 & WP6)

Impact: Viable pathways to rollout CCUS in areas with high concentrations of CO_2 emitting industries and nearby geological storage

Dissemination, communication and public engagement

Objectives:

- Understand the risks and barriers to CCUS, including those of stakeholders in NSP cluster.
- Create a short-list of recommended CCUS business models for long-term integration of CCUS in the NSP cluster
- Construct an effective narrative for CCUS in order to contribute to societal readiness and generate public support

Why are policies and business models needed?

CO_2 capture from industrial emitters

Need to remain financially competitive with sites w/o CCS – need strong revenue model and protection from some risks.

CO_2 transport operators

Need certainty of CO_2 volumes and transport fees, from emitters and/or storers (or protection from cross-chain default risks).

CO_2 storage operators

Need certainty of CO_2 volumes and storage fees. Early projects need support with CO_2 leakage liability.

CO_2 capture from power emitters

Need to have certainty on future role in power market and a guaranteed revenue from services provided.

Government and society

Need decarbonisation at lowest cost to society and minimum environmental impact. Need to understand the benefits of CCUS.

CO_2 utilisation

Need regulatory framework for CO_2 accounting and verification of climate benefits. Need development of end-use markets and likely financial support or end-use standards.

Agenda

Introduction

Risks policy must address

Business model example

CCU policy requirements

Identified risks, challenges & failure factors

WIP

Recurring factors contributing to project failures
Lack of long-term economic viability
Poor risk management
Technical integration and compatibility when scaling up from demonstration to commercial scale
Over-reliance on Government subsidies
Additional factors specific to full-chain CCUS projects
Poor management of cross-chain liabilities and poor risk ownership allocation among project stakeholders
Poor coordination of construction timescales or poor integration design between the interfaces of each CCUS segment

Category	Associated risks and challenges	C	T	U	S
Technical and operational	Technology performance uncertainty	■	□	□	□
	Technology lock-in	■	□	□	□
	Site-specific challenges	■	□	□	□
	Increased operational complexity	■	□	□	□
	Variation in CO_2 purity grade	□	■	■	■
	Maintenance of pipelines	□	■	□	■
	CO_2 storage well damage	□	□	□	■
Economic and market	High capital investment	■	■	■	■
	Capital cost uncertainty	■	■	■	■
	Opportunity cost (technology lock-in)	■	■	■	■
	Poor finance opportunities	■	□	□	□
	Energy cost uncertainty	■	■	■	■
	Long investment timescales	■	■	□	■
	Insufficient value proposition	■	□	□	□
	Reduced competitiveness	■	■	■	■
	Carbon leakage (offshoring of emissions)	■	□	□	□
	Revenue volatility	■	□	■	■
	T&S monopoly and fee uncertainty	□	□	□	■
	Long-term CO_2 storage liability	■	■	□	■
Political	**Policy and regulatory uncertainty**	■	■	□	□
	Carbon leakage and employment loss risk	□	■	□	□
	CO_2 price level and uncertainty	■	■	■	□
	Stringent conditions of government support	■	■	■	■
	Complex permitting processes	■	■	■	■
Cross chain	**Integration risk**	■	■	■	■
	Operational interface risk	■	■	■	■
	Risk allocation	■	■	■	■
	Cross-border	■	■	■	■
	Cluster / hub coordination	□	■	□	□

Legend:

C Capture
T Transportation
U Utilisation
S Storage

■ Segment predominantly affected

□ Segment less affected

Source: Element Energy as part of C4U WP6

Agenda

Introduction

Risks policy must address

Business model example

CCU policy requirements

Project example - Business model characterisation & assessment

Revenue*

Main revenue model:

- **CfD-like** mechanism (or CPF)
- **RAB-like** mechanism
- **Cost plus:** public operational payments (open book)
- **CO_2 abatement payments** (fixed or variable)
- **Green product** premium or product CO_2 taxes
- **CCS certificates** tradeable, obligated
- **Tax credits** tradeable
- **Public procurement** of low-carbon products

Supporting only:

- CO_2 price avoidance or credits
- CO_2 utilisation & EOR
- Energy performance standards
- Obligation (CCS or industrial decarbonisation)

Funding source

- Exchequer (taxpayer)
- All industrial emitters
- All national emitters
- Fossil fuel suppliers
- Gas and/or electricity consumers
- Purchasers of low carbon products (price premium)

Supporting

- CO_2 sales for utilisation eg EOR
- CO_2 tax avoidance

Risk Management

- Public loan guarantees
- Public underwriting of operational risks e.g. opex
- Stable policy / long term contracts
- Insurer / buyer of last resort
- Price floor / ceiling
- Compensation for BAU disruption
- Revenue guarantees*
- Border adjustments

Supporting cross-chain requirements:

- Contractual arrangements eg take-or-pay, interface agreements, T&S fee regulation
- Public backstops on cross-chain default
- Multiple emitters and stores

Capital

- Public grants
- Public loans
- Public equity
- Emitter equity
- Investor / JV equity
- Debt / loans (inc Green bonds)
- Multilateral funds

Ownership

- Private - emitter
- Private – other eg JV
- PPP
- Public – direct
- Public – through state-owned enterprise or SPV

Build additional elements and instruments around revenue model to mitigate risks not addressed by *revenue model* itself. Assess complete business model using step 1 & 2 criteria.

Step 1 criteria: industrial acceptability

1. Capital availability or low cost financing
2. Strength of revenue incentive
3. Industry competitiveness and carbon leakage
4. Flexibility for operational cost uncertainties
5. CO_2 price level and uncertainty
6. Simplicity and transparency for industry

Step 2 : government acceptability

1. Cost: efficiency promotion
2. Cost: ability to pass costs on
3. Policy track record
4. Speed and simplicity of implementation
5. Ongoing simplicity for government

- Applicability to industrial sectors
- Applicability to CCS phases

Source: Element Energy for BEIS, industrial carbon capture business models 2018

Business model summary example – CfD_C CO_2 certificate strike price

Revenue

- CfD_C on strike price £/tCO_2 for abated CO_2, via tradeable CO_2 certificates
- Offered contract fixed for duration but set annually for new joiners[1]

Risk mitigation

- Capital loan guarantee in scale-up
- Long term contract on strike price[2]
- ICC cost backstops/pain-gain sharing

Funding source options

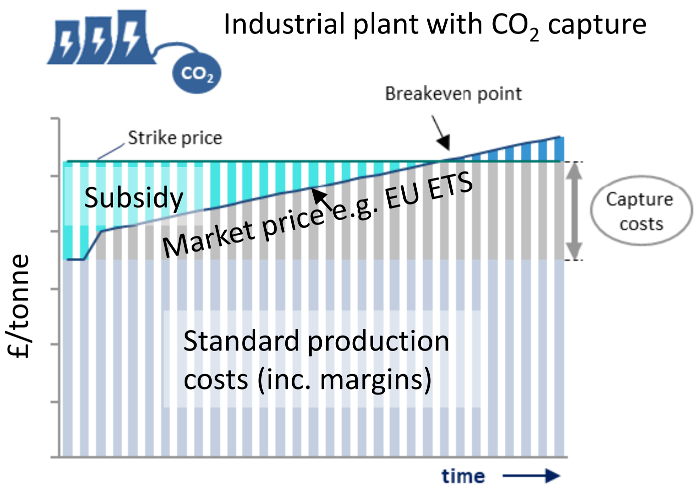
- Government: general taxation or levies eg fossil fuel suppliers

Capital

- *Roll-out*: Emitter equity & low-cost loans
- *Scale up*: grants or loan guarantees

Description & discussion

- The emitter is paid the difference between the CO_2 strike price contractually agreed (that needed to cover capture costs) and the prevailing CO_2 market price (e.g. EU ETS). For early projects, strike price may need to be high due to higher risks.
- Cost to government, if well designed, is only that required above the carbon price avoidance to compensate the emitter and protect competitiveness. Efficiency is incentivised, but costs are not passed on to consumers.
- Policy track record and applicability is high, although power CfD is on product price.



Industry criteria

- Capital availability
- Revenue strength
- Competitiveness
- Opex uncertainty
- CO_2 price
- Simplicity

Government criteria

- Cost: efficiency
- Cost: pass on
- Track record
- Implementation
- Administration
- Sectors
- Phases
- CCS specific?

Source: Element Energy for BEIS, industrial carbon capture business models 2018

1: Scale-up: negotiation on site by site basis. Roll-out: competitive bidding process.

2: Annual adjustments including linked to fuel prices or CPI-linked https://lowcarboncontracts.uk/payments

CCUS deployment: Several promising business models were identified for industrial carbon capture, drawing on comparable existing policies

Contract for difference:
CfD on CO_2 price relative to market CO_2 price (e.g. EU ETS) to provide guarantee of revenue

Cost plus:
All properly incurred ICC operational costs are reimbursed through taxpayer funding

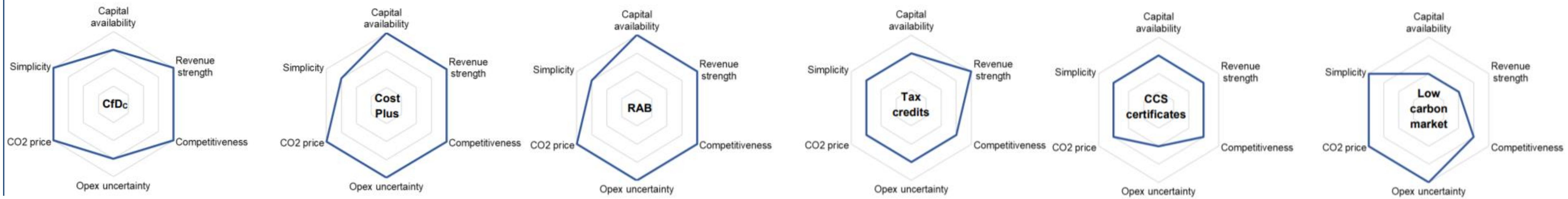
Regulated asset base:
Public regulation allows costs to be recovered through product prices e.g. of Hydrogen

Tradeable tax credits:
CCS tax credits awarded $/t$CO_2$ to reduce firms tax liability (e.g. 45Q) or trade with other firms.

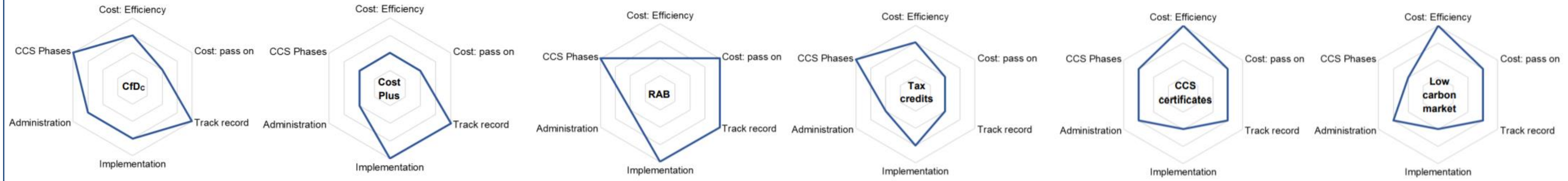
CCS certificates:
Certificates representing tCO_2 abated through CCS, which can be traded and emitters have an obligation.

Low carbon market:
End-use regulation e.g. on buildings to create a low carbon market & achieve product premium

Acceptability to industry evaluation



Acceptability to government evaluation



Key messages

Industrial carbon capture

- The key challenge for industrial carbon capture is providing the **revenue level and certainty** to incentivise industry to decarbonise and unlock capital whilst protecting it from carbon intensive competition, and therefore prevent carbon leakage.
- **There are a number of available mechanisms** to support the deployment of industrial carbon capture. The key to a successful mechanisms is balancing the private and public sector requirements. A number of key learnings can be taken from projects such as Longship, Lake Charles Methanol and Porthos e.g. financial structure, CCUS value chain construction and use of existing assets.
- **Each of the revenue models requires support from a suite of risk management instruments** to ensure risks are addressed where possible. This is particularly important for incentivising deployment of early projects where the private sector cannot bear these risks.

CCUS

- In the longer term as CCUS clusters grow and costs and risks reduce, **CCUS may be able to transition to an unsubsidised end-state**. This assumes either global action on climate or border adjustments for product carbon intensity.
- CCUS requires a business model for the other aspects of the chain, such as CO_2 transport and storage or utilisation. **The integration of these business models is key**, with cross-chain risks significant for early or isolated projects.
- **The Netherlands has implemented a mechanisms in SDE++**[1] (similar to a CfD), which is likely to form part of the North Sea Port business models. The NSP will be explored in more detail in our work in the coming 2 years.

1 the government pays the difference between the cost price of a technology and the market price of carbon abatement, expressed in euros per metric tonne of CO2. It guarantees to do this for 12 or 15 years.

Agenda

- Introduction
- Risks policy must address
- Business model example
- **CCU policy requirements**

Revenue from CCU products:
challenges of market uptake & enabling interventions

Competitiveness & Market Potential: products from CO_2 utilisation need to compete with existing products and penetrate markets

Challenges to successful uptake of CCU products

Demonstrating product suitability:

- Technologies need to be demonstrated at scale to gain investor confidence
- Products need to meet existing standards and regulations. This can be a lengthy and expensive process. Prescriptive standards may prevent approval.
- Some markets are highly conservative needing further demonstrations over many years.

Developing market interest and product demand:

- Procurers may lack awareness or engagement with their Scope 3 emissions.
- Procurers may not have awareness of CCU products or the benefits of CCU. There may be a lack of clarity on how these benefits may be realized through carbon accounting.
- Consumer perception could be a barrier if not managed well, or a driver.
- Market drivers are typically not sufficient to justify cost premiums for CCU products.

Achieving cost-competitiveness:

- CCU products can be significantly more expensive than conventional fossil-based products (which may be in recite of subsidies).
- However, a select few routes are driven by cost-savings or improving the value of products.
- Avoidance of fees or compliance with regulations could become a driver if more ambitious incentives or targets are imposed.

Interventions to enable success

- **Funding for innovation & demonstration projects.**
- **Facilitating testing & approvals processes.**
- **Updating of standards to be performance based.**

- **Increasing awareness and reporting of lifecycle & Scope 3 emissions.**
- **Clarifying carbon accounting for CCU products.**
- **Use of mandates or standards to increase demand for lower emission products.**

- **Funding of linked projects such as renewables, green hydrogen and carbon capture to lower costs.**
- **Introducing policies to level the field by recognizing sustainability benefits (performance based).**

Support for CCU: examples of existing or adaptable support mechanisms

Research & Demonstration Funding

- Funding programmes in the EU (H2020, Innovation Fund), US and member states.
- Private investment initiatives and competitions such as Carbon Xprize

Low Emission Fuels Standards / Targets

- Blending obligations for road transport (EU RED II) and aviation fuels (e.g. Norway)
- Minimum standards (e.g. Californian Low-Carbon Fuel Standard)

Level Field Mechanisms & Subsidies

- Carbon pricing (ETS or carbon tax)
- Operational subsidies such as Contract for Difference (e.g. Netherlands SDE++)

Testing, Approvals & Certifications

- US Clearing House facilitating aviation fuel approvals
- Sustainability Certification Schemes & product labelling

Procurement Guidelines

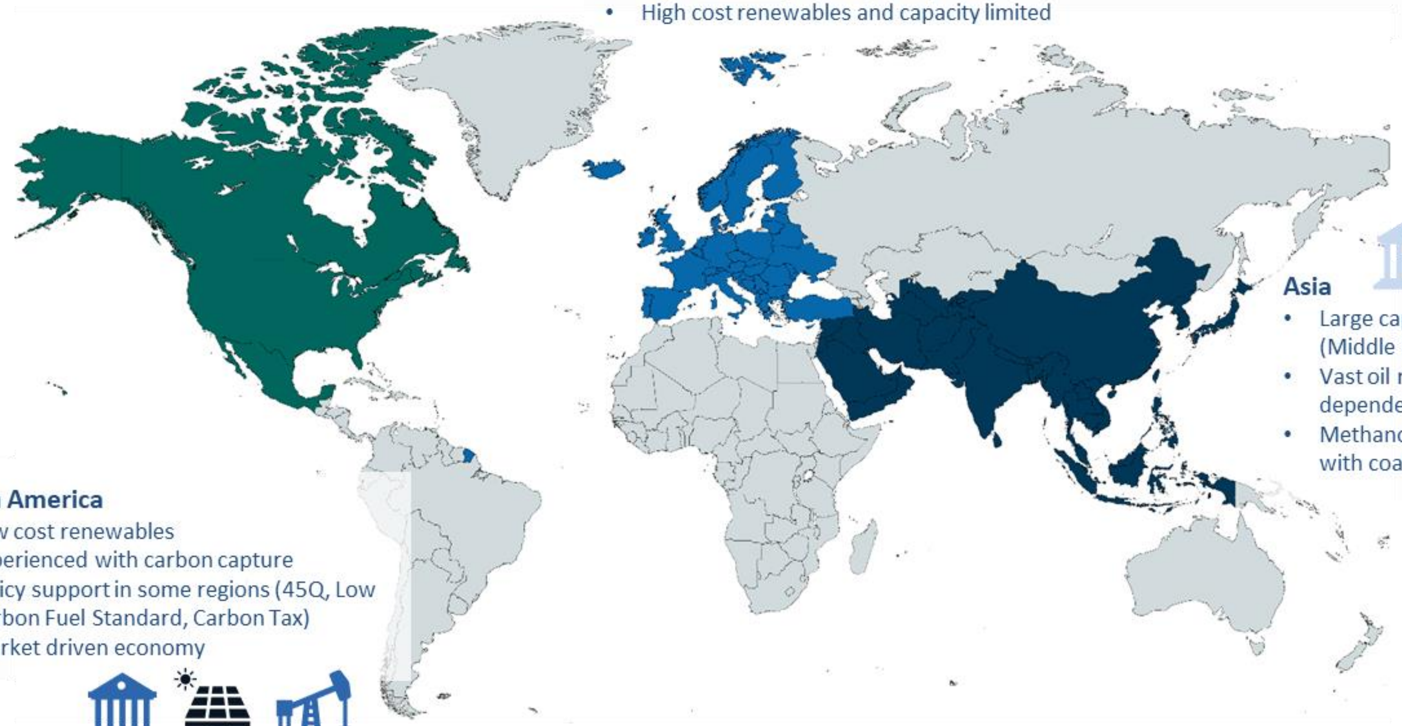
- Standards for public infrastructure projects (e.g. UK BREEAM rating)
- Tender evaluation (e.g. Netherlands CO_2 performance ladder)

Company Monitoring & Reporting

- Emission reporting obligations (government & investor driven)
- Knowledge sharing & guideline development

Drivers, barriers and enablers for CCU can vary regionally. There may be local niche opportunities where CCU becomes favourable.

Europe
- Strong climate ambition and policy support (RED II, EU ETS, Carbon Tax)
- Innovation encouraged (funding & grants)
- Lack of fossil reserves (net importer)
- High cost renewables and capacity limited



Asia
- Large capacity for low cost renewables (Middle East)
- Vast oil reserves and economic dependence on exports (Middle East)
- Methanol economy in China and India, with coal reserves and coal-to-chemicals

North America
- Low cost renewables
- Experienced with carbon capture
- Policy support in some regions (45Q, Low Carbon Fuel Standard, Carbon Tax)
- Market driven economy

Policy & Regulatory Support (limited - **ambitious**)
Deployment of Renewables (expensive - **cheap**)
Fossil Resources (limited - **vast**)

Source: Element Energy analysis as part of ongoing CCU work

Thank You!

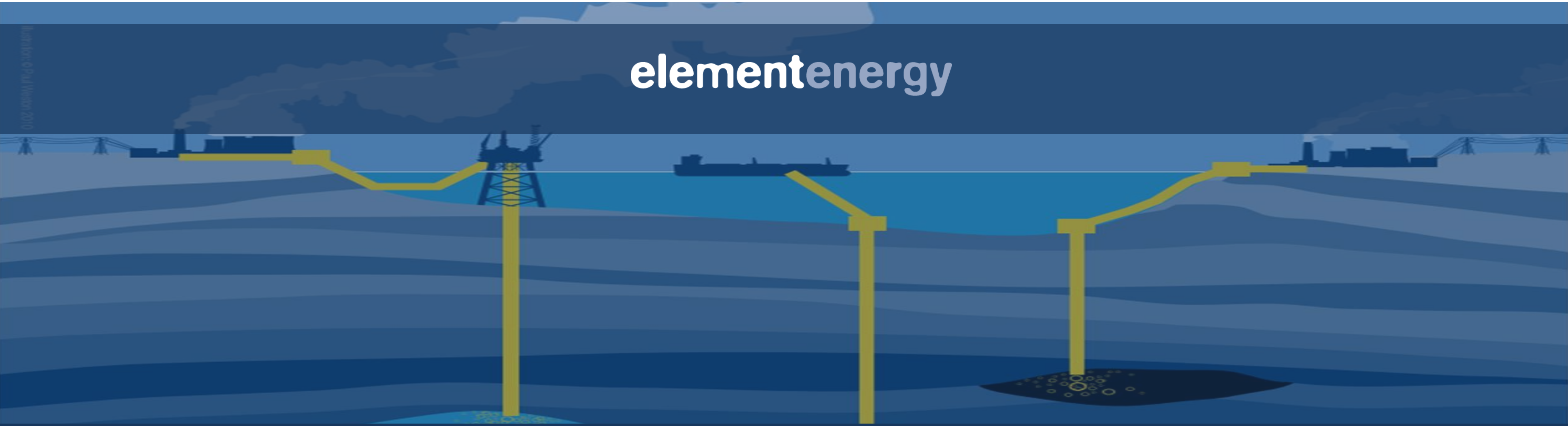
Thank you for your listening!

Any questions?

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884418

Element Energy is a leading low carbon energy consultancy working in a range of sectors including industrial decarbonisation, carbon capture utilisation and storage (CCUS), hydrogen, low carbon transport, low carbon heat, renewable power generation, energy networks, and energy storage. Element Energy works with a broad range of private and public sector clients to address challenges across the low carbon energy sector.

For further information please contact:
CCUSindustry@element-energy.co.uk



Perception of CO_2-based fuels and their production in international comparison

Linda Engelmann, M.A.
HCIC | Chair of Communication Science
RWTH Aachen University

engelmann@comm.rwth-aachen.de

Introducing the project

Closing the loop: from CO_2 to fuel

Direct electrocatalytic conversion of CO_2 into chemical energy carriers in a co-ionic membrane reactor

ecocoo.eu

Project aim

- set up a CO_2 conversion process using renewable electricity and water steam to directly produce synthetic jet fuels with balanced hydrocarbon distribution to meet the stringent specifications in aviation
- process is compact, modular – quickly scalable – and flexible, thus, process operation and economics can be adjusted to renewable energy fluctuations
  → technology will enable to store more energy per processed CO_2 molecule and therefore to reduce GHG emissions per jet fuel ton produced from electricity at a substantial higher level

Consortium

Integration of societal acceptance and perception into sustainable technology development

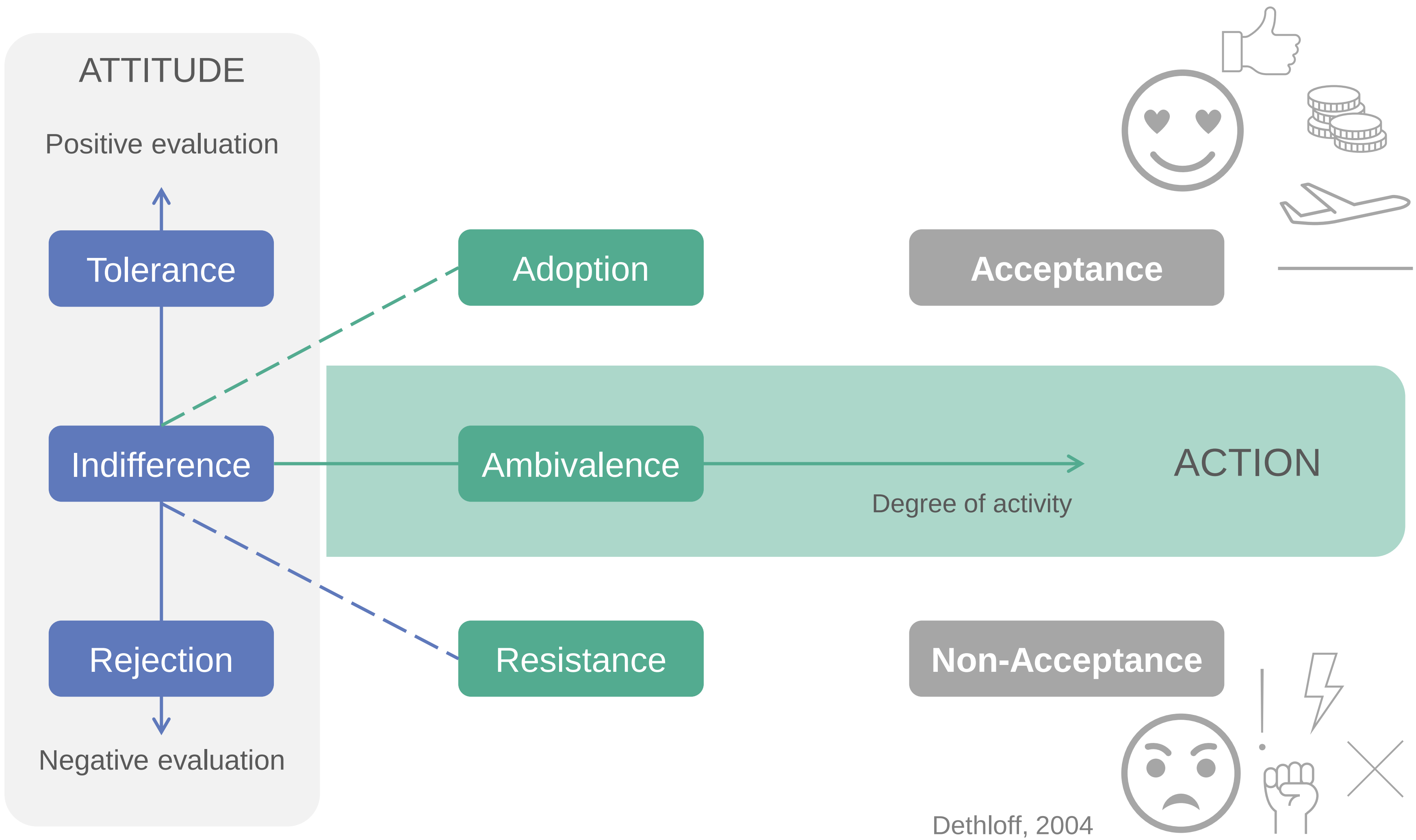
Consideration of public perceptions and acceptance from the very beginning of the developmental process

Informing technical designers about acceptance barriers

Education of the public and increase of awareness

Development of communicative strategies

How do we define acceptance?

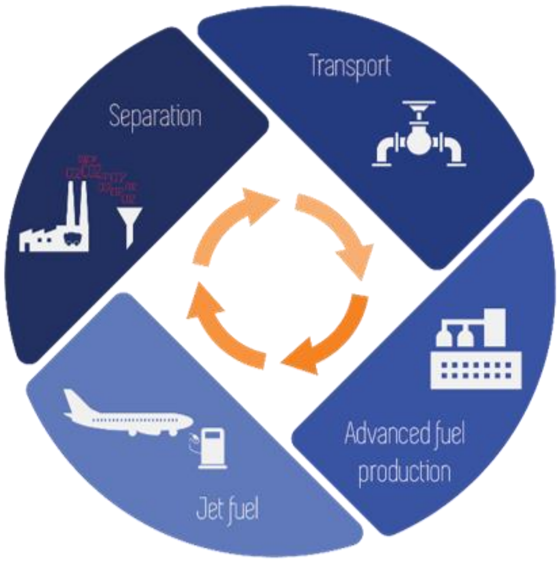


Dethloff, 2004

Objects of investigation
– Societal perception of CO_2-based fuels

Previous Research

- Protest potential against CCS is impacted by risk and benefit perceptions of CCS (Wallquist et al., 2012)
- Perception of mattresses as a CO2-based product is linked to health and environmental risk perception (Arning et al., 2018)



- Technical *infrastructure* and *production processes*
- CO_2-based jet fuel as *end-product*

Target groups
laypeople, technical experts, industrial stakeholders, policy makers

Methods
Mixed method approach
interviews, surveys

International survey on CO_2-based aviation fuels

Sample (*N* = 2.187)

Germany (*n* = 543)

M = 45 years
SD = 15.2 years

49.9% female
50.1% male

Netherlands (*n* = 549)

M = 44.8 years
SD = 15 years

50.8% female
49.2% male

Spain (*n* = 545)

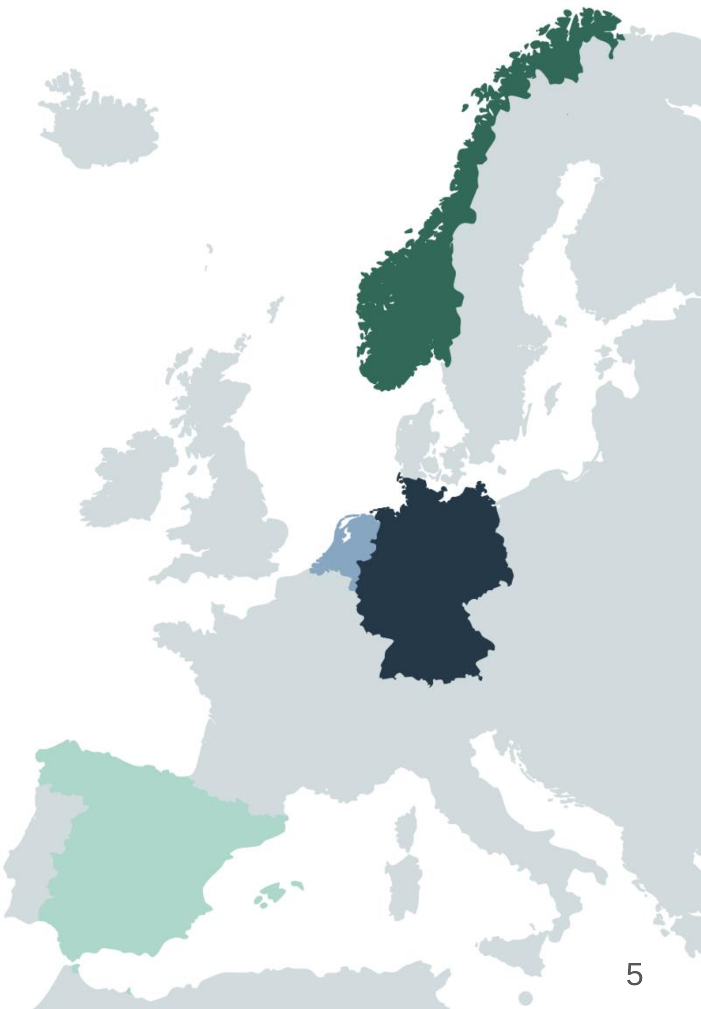
M = 45.4 years
SD = 12.9 years

54.9% female
45.1% male

Norway (*n* = 550)

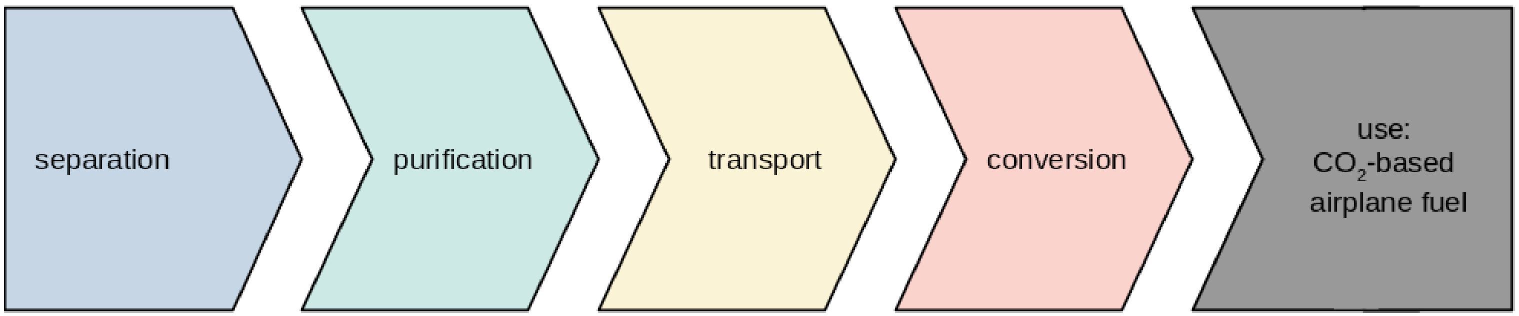
M = 45 years
SD = 14.4 years

52% female
48% male

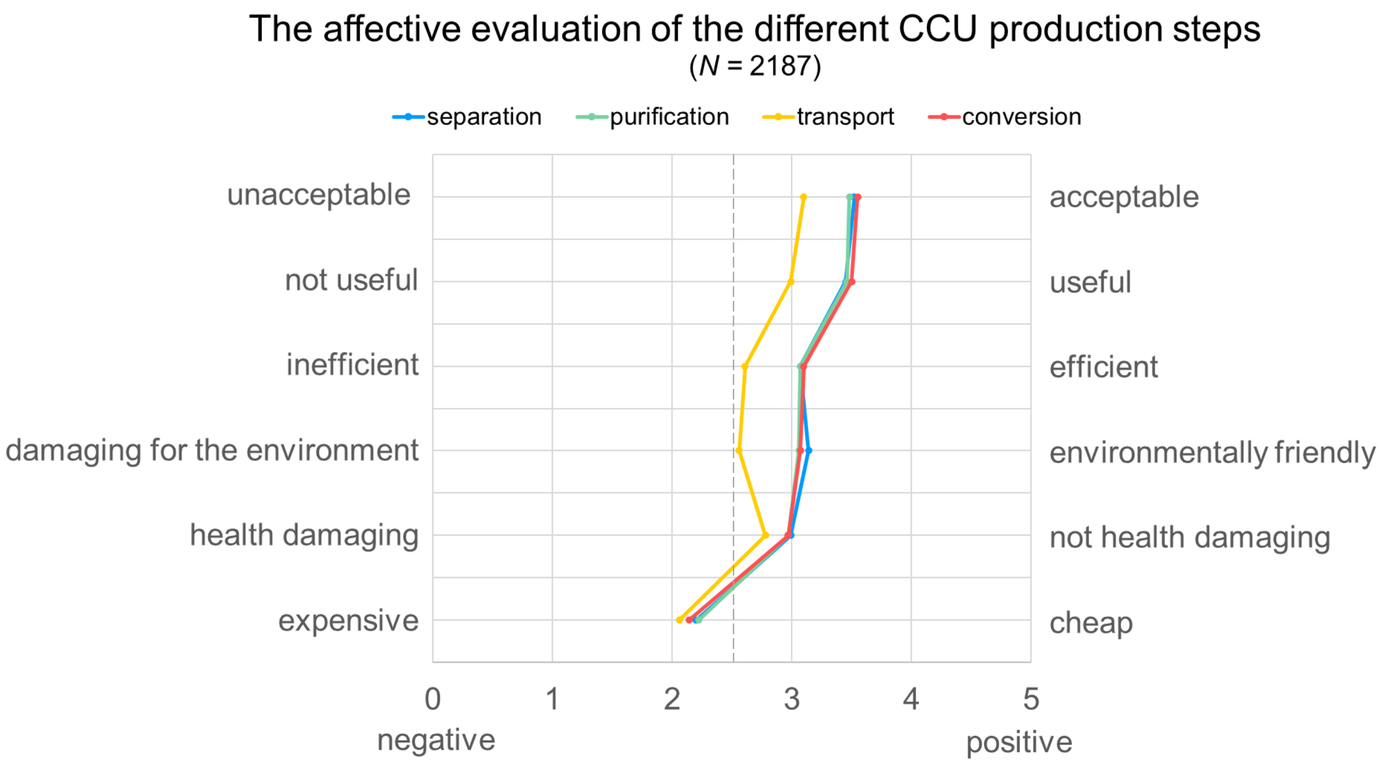


Assessment of production and product

Production CO_2-based fuel using CCU

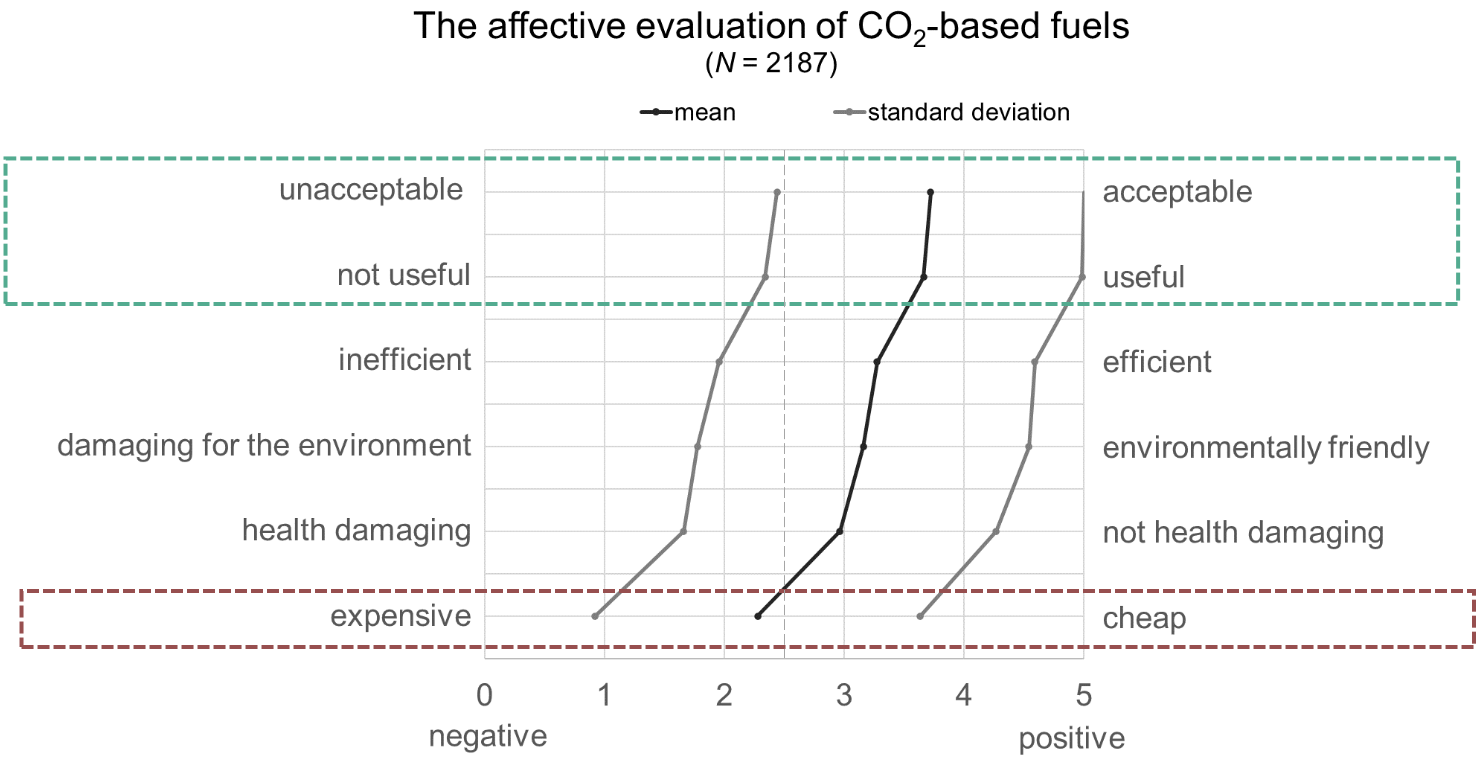


Differences in evaluation for production steps



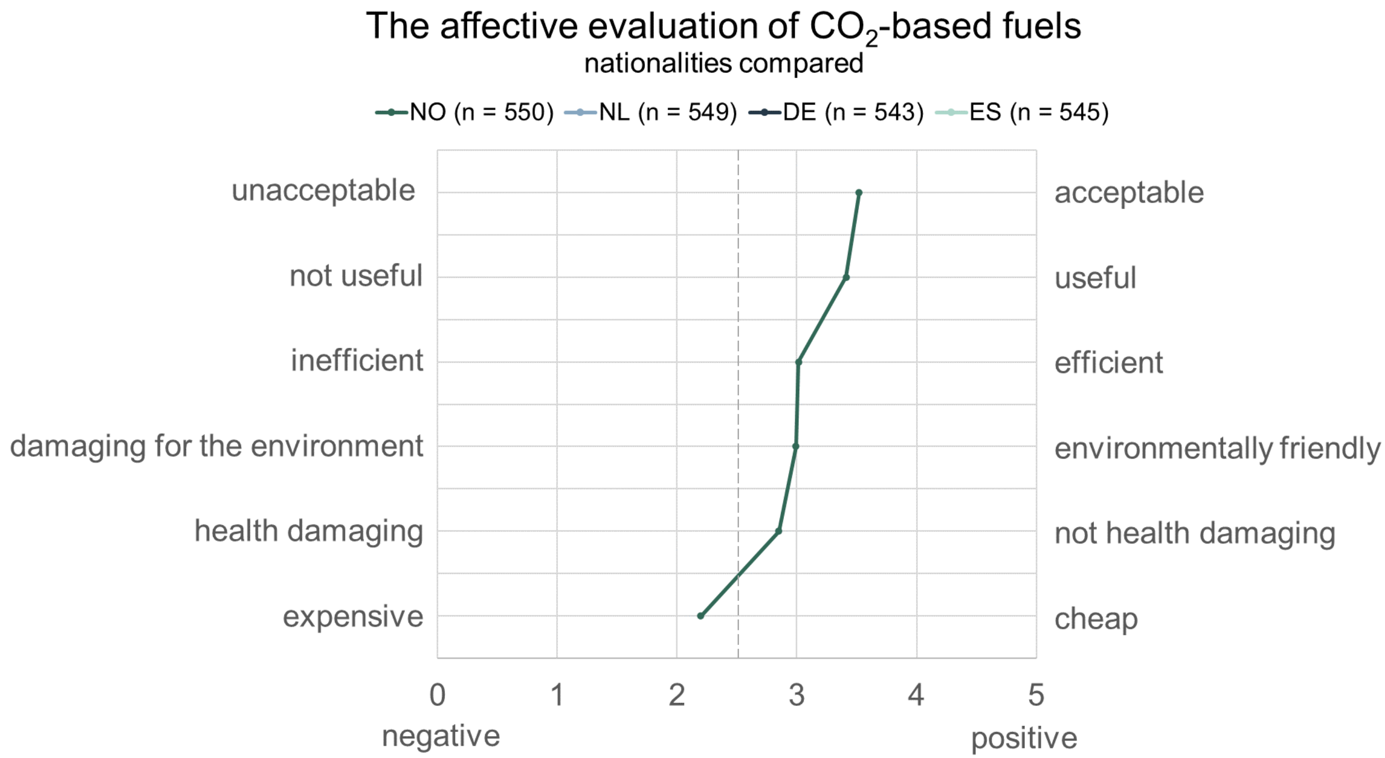
Generally, the production steps are perceived as being acceptable and useful. However, people do think it will be expensive.

Evaluation of the end-product CO_2-based jet fuel



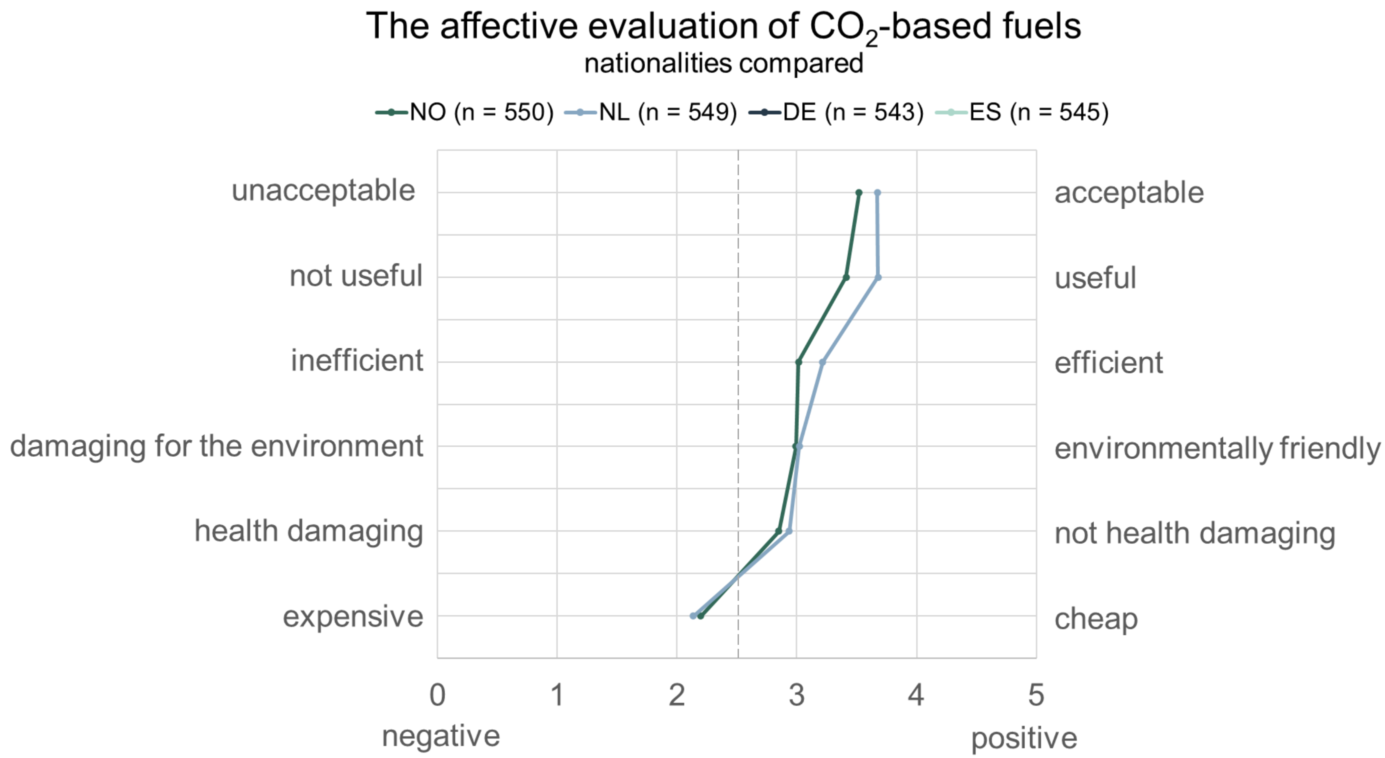
Perception of CO_2-based fuel:
Rather acceptable, useful, efficient, environmentally and health friendly, assessment of price as rather expensive

Evaluation of the end-product CO_2-based jet fuel
National differences



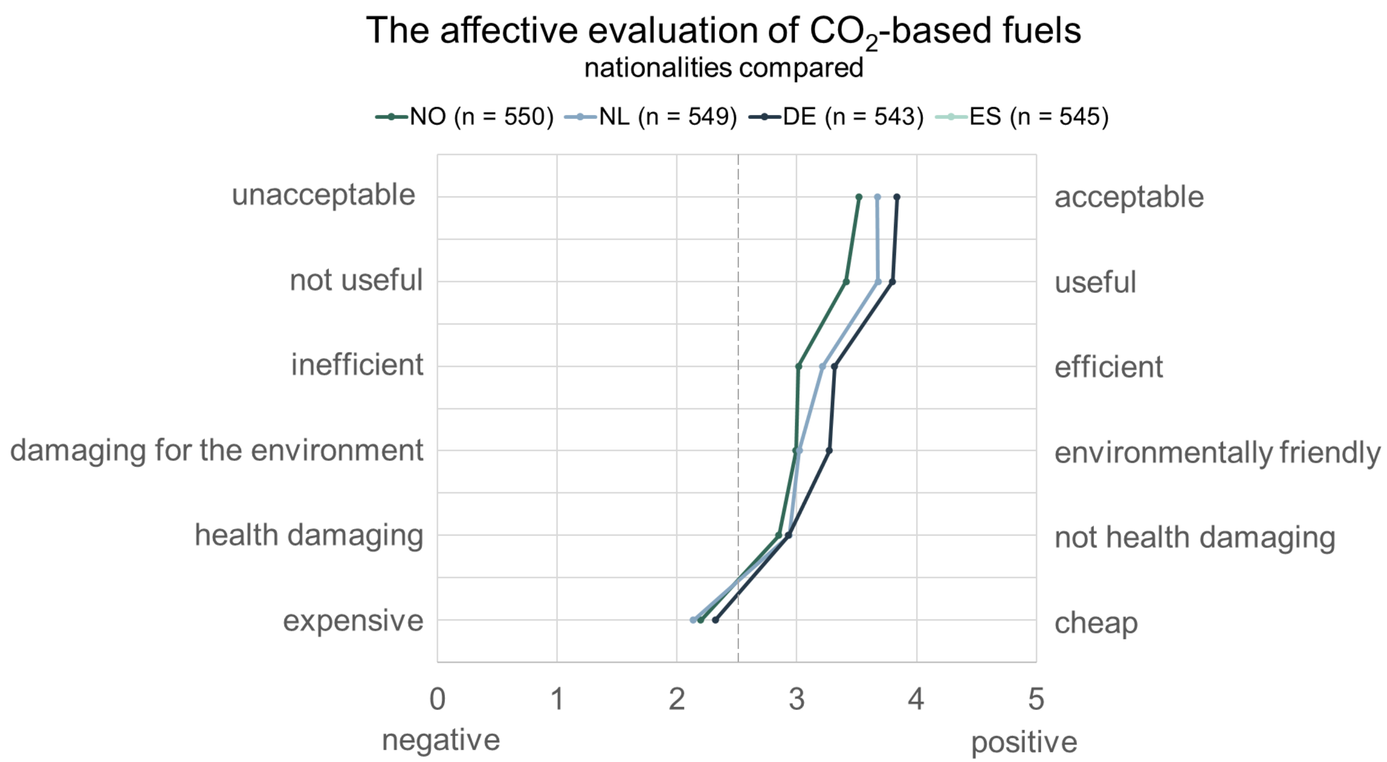
The affective evaluation of the end-product of CO_2-based fuels was least positively perceived by the Norwegians,...

Evaluation of the end-product CO_2-based jet fuel
National differences



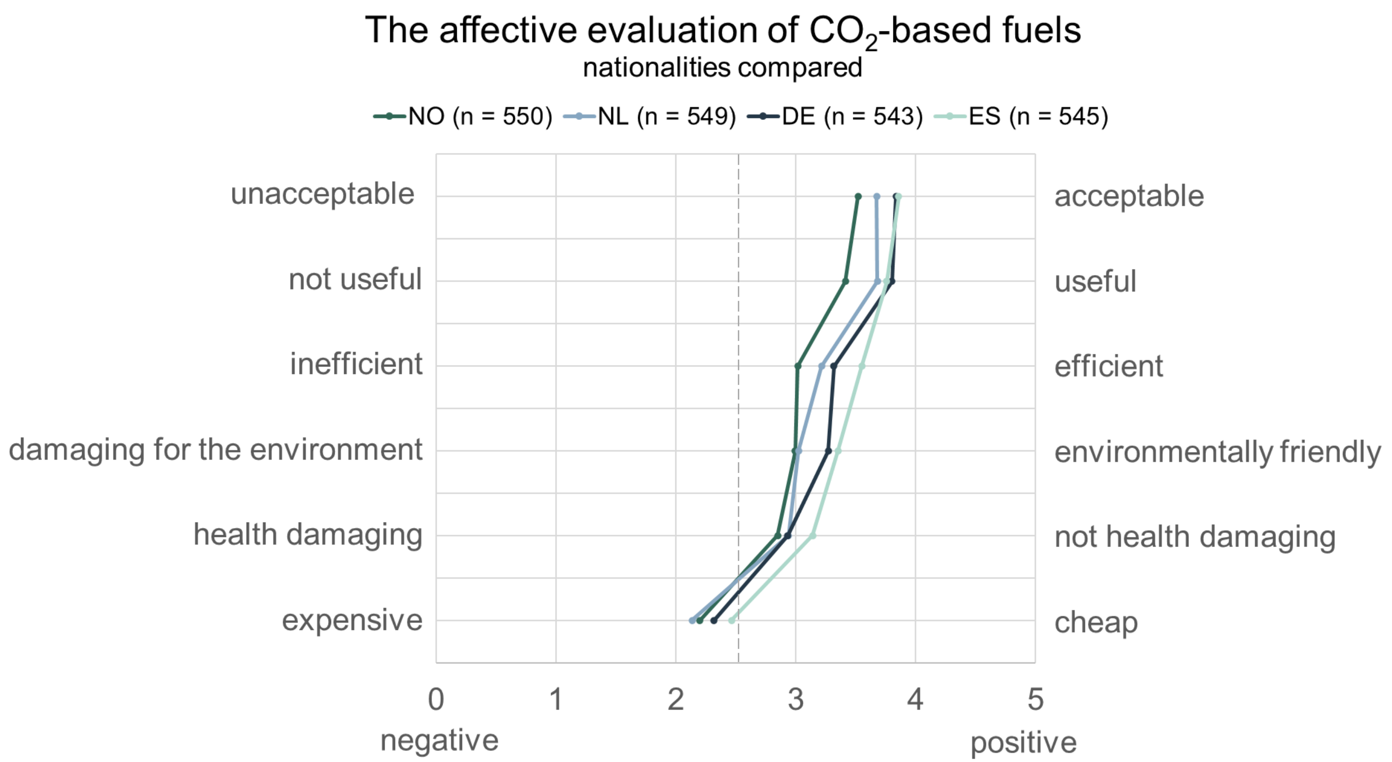
The affective evaluation of the end-product of CO_2-based fuels was least positively perceived by the Norwegians, followed by the Dutch,…

Evaluation of the end-product CO_2-based jet fuel
National differences



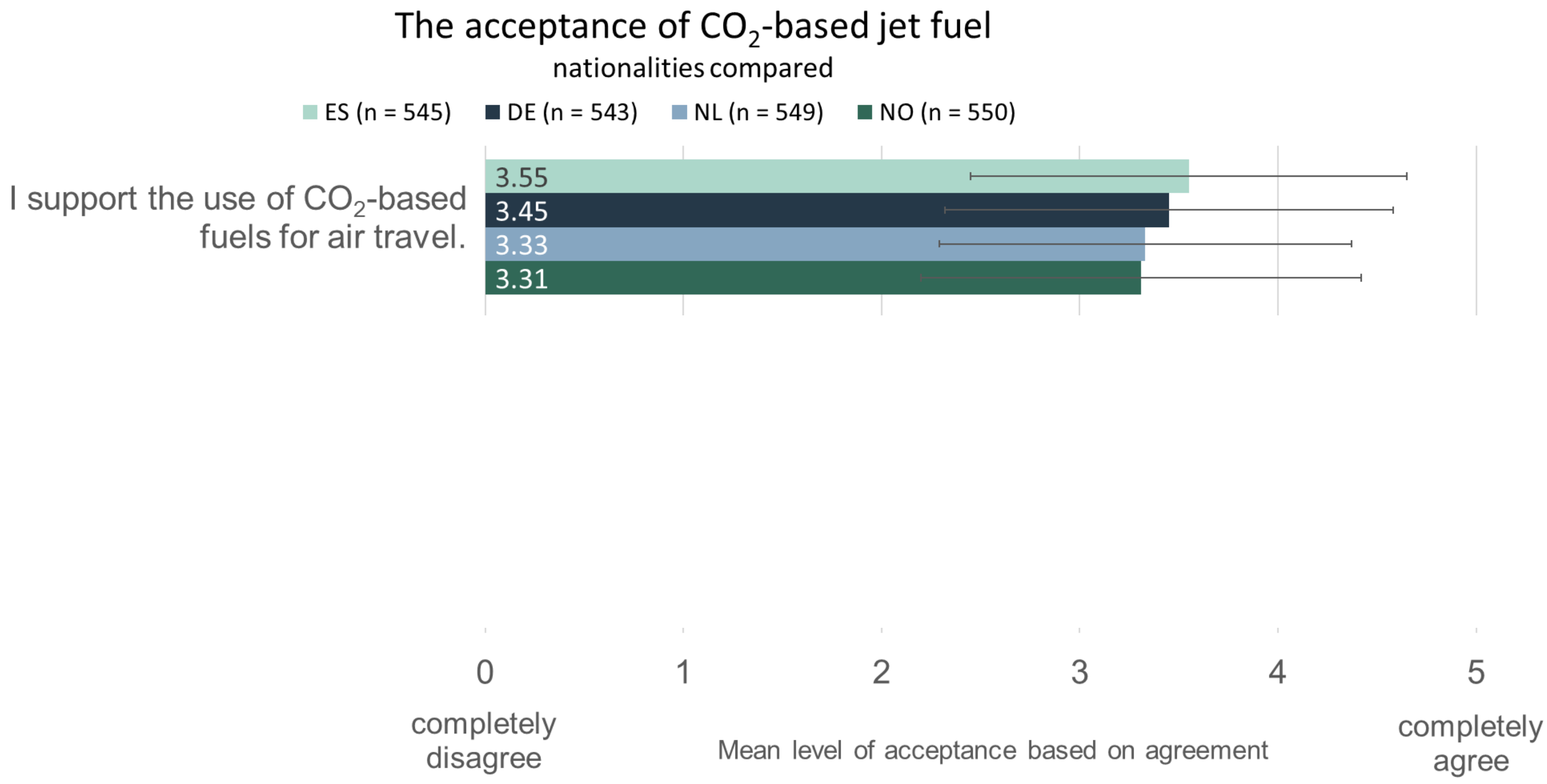
The affective evaluation of the end-product of CO_2-based fuels was least positively perceived by the Norwegians, followed by the Dutch, the Germans,…

Evaluation of the end-product CO_2-based jet fuel
National differences

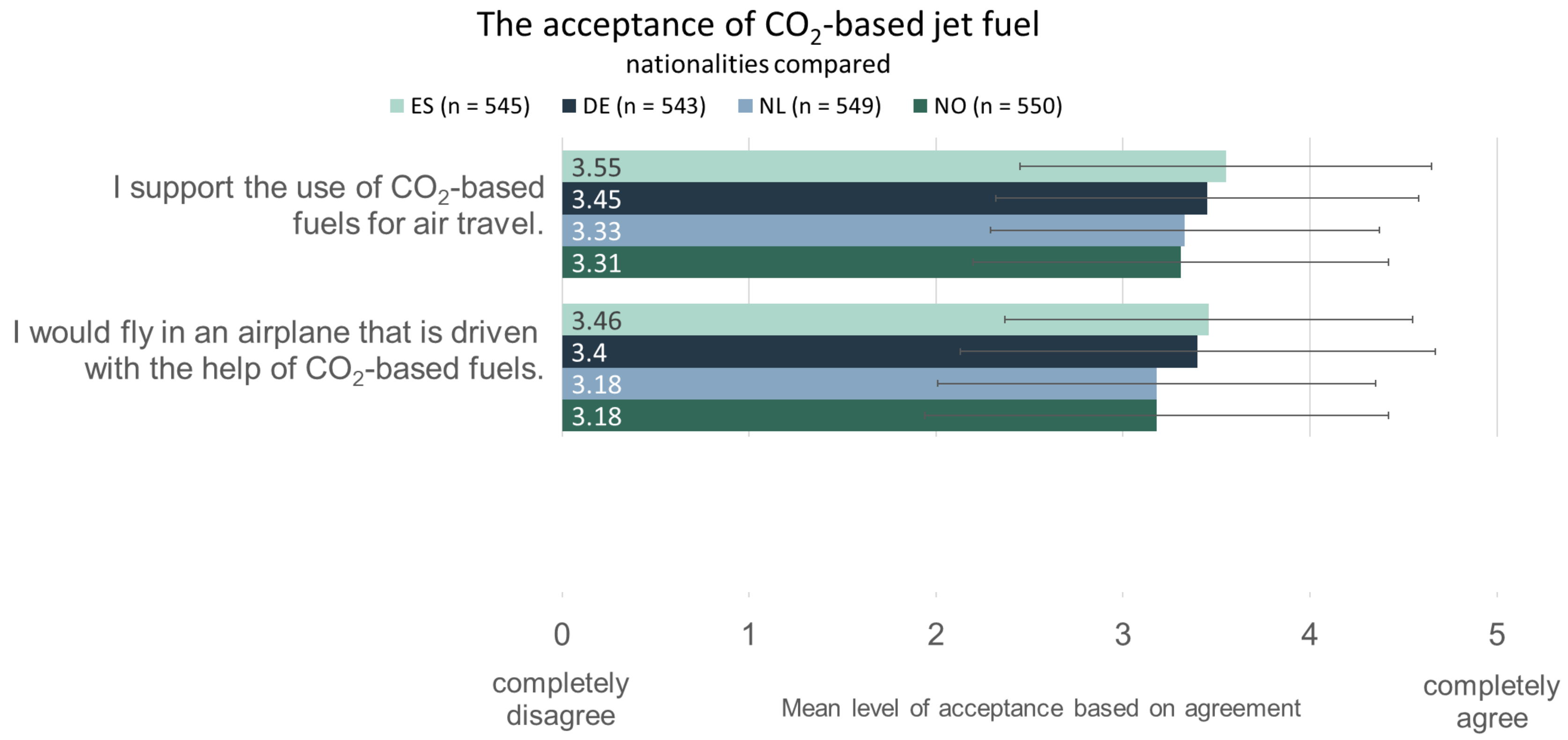


The affective evaluation of the end-product of CO_2-based fuels was least positively perceived by the Norwegians, followed by the Dutch, the Germans, and finally the Spaniards.

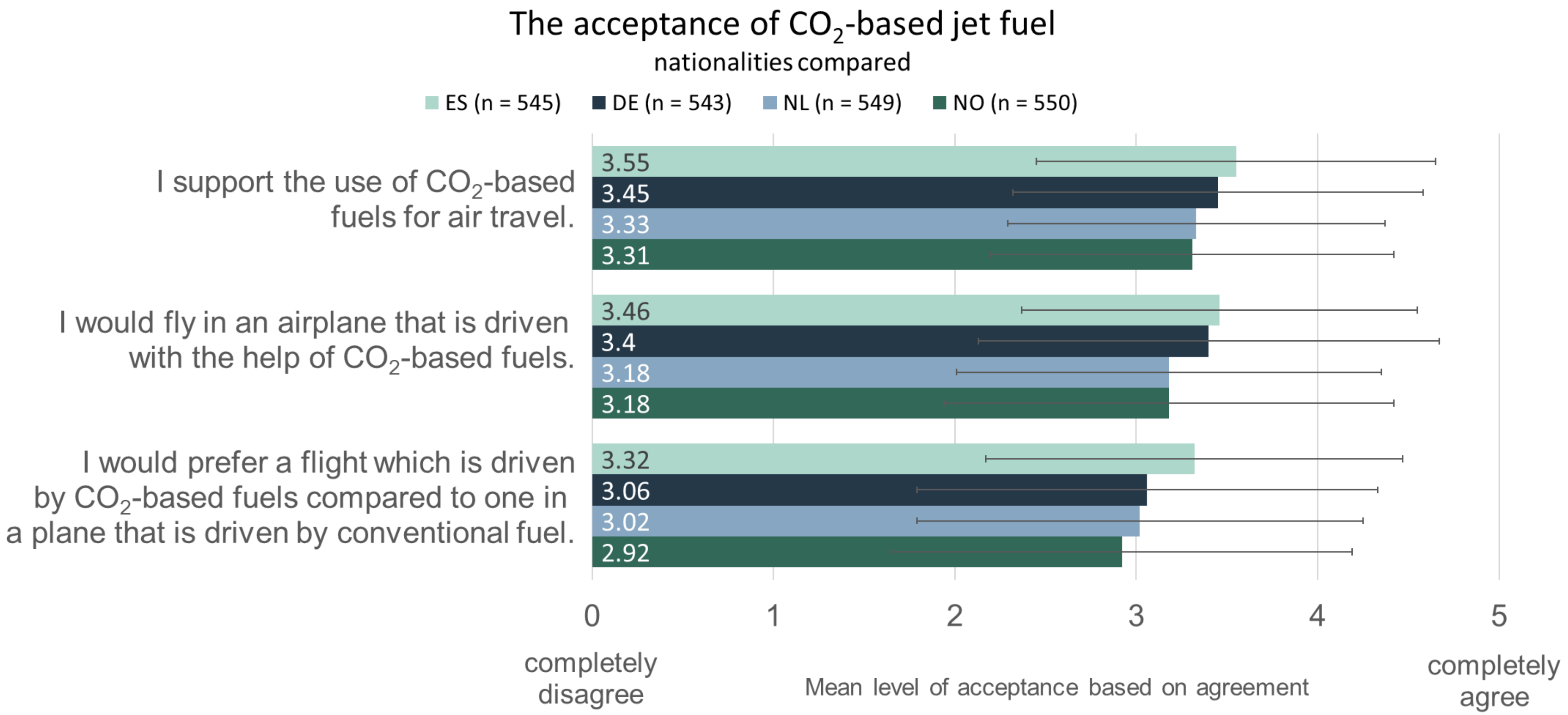
Acceptance of CO_2-based jet fuel
National differences



Acceptance of CO_2-based jet fuel
National differences

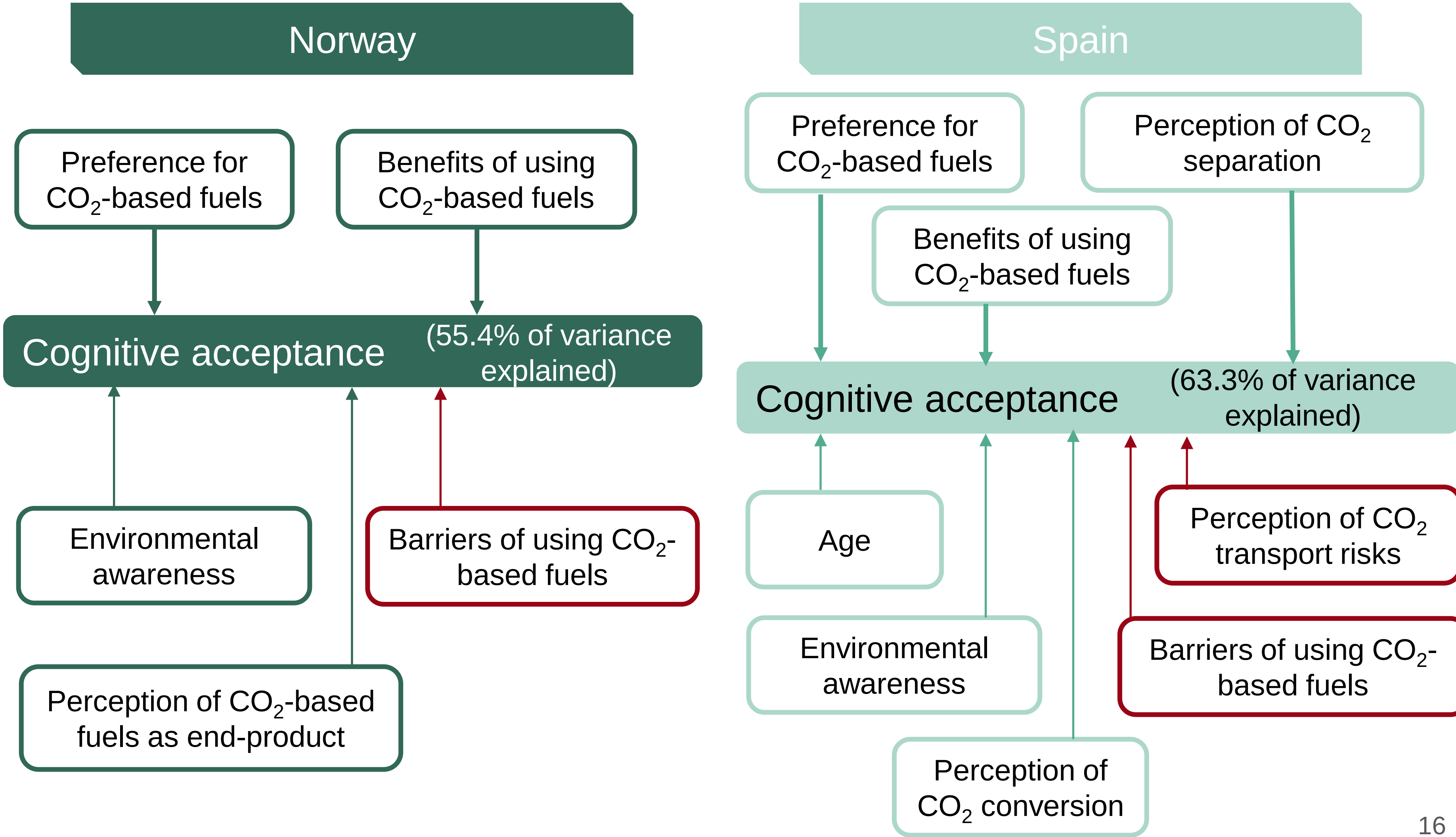


Acceptance of CO_2-based jet fuel
National differences

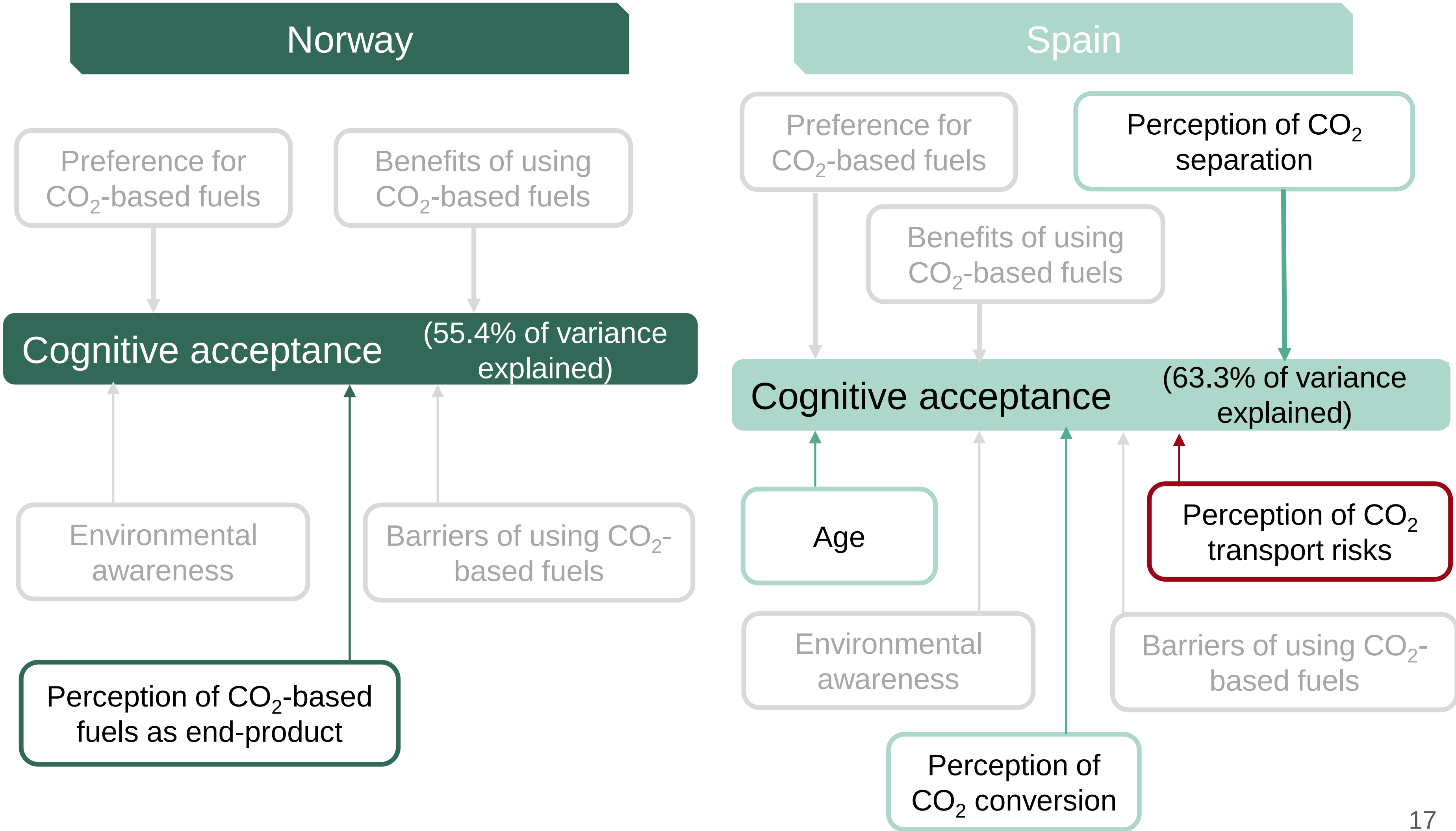


The greatest approval and willingness to use CO_2-based fuel existed among Spanish participants, followed by Germans, Dutch and Norwegian people.

Differences in acceptance influencing factors

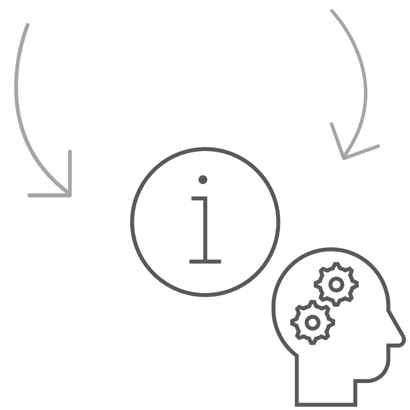


Differences in acceptance influencing factors

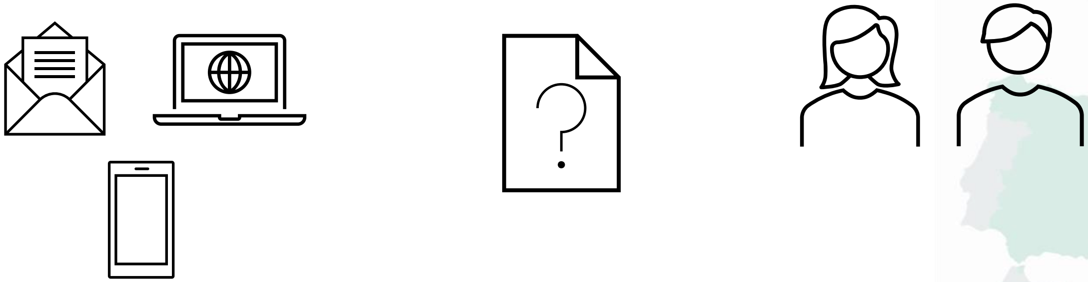


Outlook: Communication and information strategies

What increases or decreases acceptance?



What informative and communicative needs do different groups have?



Thank you
for your attention!

Human and societal dimensions

Dr Niall Dunphy, University College Cork @NPDunphy

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884266

INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILIZATION
TU/E - EINDHOVEN - 16-17 FEBRUARY 2021

University College Cork, Ireland
Coláiste na hOllscoile Corcaigh

REALISE project overview

- Demonstrating a refinery-adapted cluster-integrated strategy to enable full-chain CCUS implementation
- Horizon 2020 funded project (LC-SC3-NZE-5-2019-2020)
- 3-year duration – commenced May 2020
- Working to develop means to capture up to 90 % of CO_2 from multiple sources in operating refineries

www.realiseccus.eu @realise-ccus

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884266

Socio-political dimension of decarbonization

- Achieving the decarbonization of Europe is a key goal of the European Green deal.
- The required energy and industrial transition will both necessitate, and result in, a substantial societal transformation.
- Citizens have a crucial role to play in this transition, indirectly by accepting, supporting or resisting changes and thus influencing other policy actors or directly by consenting or refusing policy options in democratic decision-making processes.

Mullally, G.M., Dunphy, N.P., & O'Connor, P. (2018). Participative environmental policy integration in the Irish energy sector. Environmental Science & Policy, 83, 71–78. https://doi.org/10.1016/j.envsci.2018.02.007

Socio-political considerations within REALISE

- The technical and geological aspects of a CCS project are of course the primary focus of the planning and implementation phases.
- However, REALISE recognizes the importance of understanding (and appreciating) the social context of prospective CCS projects.
- Specific package of work which seeks to develop and in-depth understanding of the societal, socio-political and commercial contexts of CCS deployment.

WP4 Societal, socio-political and commercial context

Task 4.1 Education and public engagement best practice

Review of EPE practices

Task 4.2 Social acceptability, societal impact

Co-development and trialing of EPE programme

Task 4.3 Socio-political context analysis

Exploring socio-political lessons learned from global CCS projects

Task 4.4 Industrial context analysis

Engagement of key CCS actors through an industry club

Task 4.5 Public outreach activities and life-long learning

Contribute to improved societal readiness through outreach

Task 4.6 Synthesis report on societal readiness

T4.1 Education & public engagement best practice

- Comprises a critical review of education and public engagement (EPE) associated with large energy and related infrastructure.
- It is intended to work towards development of a framework for social acceptance of deploying CCS at an industrial site.
- Key examples of EPE identified through a literature search and via partners' networks using a snowballing approach.

T4.1 Education & public engagement best practice

- Seven EPE case studies characterised through a comprehensive desk study coupled with use of targeted informants.
  - CO2CRC Otway Project, Australia
  - Jänschwalde CCS Project, Germany
  - San Cristóbal Mine, Bolivia
  - Block Island Wind Farm, USA
  - Portsmouth Energy Recovery Facility, UK
  - Barendrecht CCS Project, Netherlands
  - Tomakomai CCS Demonstration Project, Japan
- The resultant report details the case studies, outlines methods adopted, explores key challenges, and presents best practices.

Need for acceptance

- The deployment of the major infrastructure needed to realise the required energy and industrial transition can only be successful with social acceptance.
- This means acceptance by the public generally (of the technology), but also, and critically acceptance by the community which will play host to the infrastructure.
- However, the strong public opposition faced by many projects threatens to significantly slow down this transition

Dunphy, N. P., Revez, A., Gaffney, C., & Lennon, B. (2017). Intersectional Analysis of Perceptions and Attitudes Towards Energy Technologies. Deliverable 3.3 of the ENTRUST H2020 project. https://doi.org/10.5281/zenodo.3479301

Social acceptance … (or)

- The term ‘*social acceptance*’ with respect to infrastructure deployment, often implies (whether by design or otherwise) a passive acquiescence of a decision that has already been made.
- Such activities are usually concerned more with advocacy rather than decision-making or decision-making processes.
- So called DAD Model - Decide, Announce, Defend
- (or Decide, Announce Defend, Abandon … DADA !)

Dunphy N.P., Lennon, B., Quinlivan, L., Velasco Herrejon, P., Curran, R. (2021). Critical review of Education and Public Engagement initiatives. Deliverable 4.1 of the REALISE Horizon 2020 project.

(or) … societal acceptability

- On the other hand, ‘*social acceptability*’ refers to a project itself, it infers an effort to design (and implement) a project to be (more) agreeable to social stakeholders.
- It suggests (and arguably requires) a more participatory approach.
- This is an implied acknowledgement of societal stakeholders’ legitimacy, provision for them to be earlier, and understanding that they would (be allowed to) provide real input into decision-making.

Dunphy N.P., Lennon, B., Quinlivan, L., Velasco Herrejon, P., Curran, R. (2021). Critical review of Education and Public Engagement initiatives. Deliverable 4.1 of the REALISE Horizon 2020 project.

Acceptability … ‘fairness’

Perceptions of fairness play a crucial role in determining the social acceptability of infrastructure projects.

- Procedural justice: the way in which the process is structured and implemented.
- Distributional justice: how benefits and ills of the project are distributed .
- Recognition justice: acknowledgement, recognition and respect.

Lennon, B., Dunphy, N. P., & Sanvicente, E. (2019). Community acceptability and the energy transition: a citizens’ perspective. Energy, Sustainability and Society, 9(35). https://doi.org/10.1186/s13705-019-0218-z

Jenkins, K., McCauley, D., Heffron, R., Stephan, H., & Rehner, R. (2016). Energy justice: A conceptual review. Energy Research & Social Science, 11, 174–182. https://doi.org/10.1016/j.erss.2015.10.004

Examples of lessons from T4.1 …

1. You cannot engage too early

- Early and open channels of communication with the public helps build mutual trust between process leaders and the community.
- Projects benefit when stakeholders across all groups are involved in the process.
- Ideally, the local community should be involved in the process of location selection, permitting, and policy-making, as soon as a project is proposed

Dunphy N.P., Lennon, B., Quinlivan, L., Velasco Herrejon, P., Curran, R. (2021). Critical review of Education and Public Engagement initiatives.
Deliverable 4.1 of the REALISE Horizon 2020 project.

Examples of lessons from T4.1 …

2. Value of community liaisons

- Useful to hire staff who either already have good relations with local communities, or who have the skills to develop trusting relationships with communities.
- Having someone who is a ‘known entity’ with at least some members in the local community is vital in building trust.
- Can also ensure issues can be dealt with promptly and before they evolve into problems.

Dunphy N.P., Lennon, B., Quinlivan, L., Velasco Herrejon, P., Curran, R. (2021). Critical review of Education and Public Engagement initiatives. Deliverable 4.1 of the REALISE Horizon 2020 project.

Examples of lessons from T4.1 …

3. Advantages of blended approach to communication

- Complement official formal communication with informal modes to ensure effective outreach and build/maintain trust with communities
- A blended approach to communication can contribute to fostering what Dwyer and Bidwell (2019) describe as a “chain of trust” between the process leaders and local stakeholders.

Dunphy N.P., Lennon, B., Quinlivan, L., Velasco Herrejon, P., Curran, R. (2021). Critical review of Education and Public Engagement initiatives. Deliverable 4.1 of the REALISE Horizon 2020 project.

Dwyer, J., & Bidwell, D. (2019). Chains of trust: Energy justice, public engagement, and the first offshore wind farm in the United States. Energy Research and Social Science, 47(January), 166– 176. https://doi.org/10.1016/j.erss.2018.08.019

Examples of lessons from T4.1 …

4. First impressions count

- Build trust through early, open & responsive communication with communities.
- Actions are interpreted through the lens of relationships – a poor relationship could lead actions to be seen as hostile, whereas a hands-off approach might lead to perceptions of having something to hide.

Dunphy N.P., Lennon, B., Quinlivan, L., Velasco Herrejon, P., Curran, R. (2021). Critical review of Education and Public Engagement initiatives. Deliverable 4.1 of the REALISE Horizon 2020 project.

Examples of lessons from T4.1 …

5. Provide good quality information

- Availability of high-quality tailored information builds trust and pre-empts issues.
- Effective (and trusted) communications promotes credibility of both the project itself and the developer.
- Important to develop an understanding of target audiences and implement a communications strategy which reflects their cultural and other specificities.

Dunphy N.P., Lennon, B., Quinlivan, L., Velasco Herrejon, P., Curran, R. (2021). Critical review of Education and Public Engagement initiatives. Deliverable 4.1 of the REALISE Horizon 2020 project.

Examples of lessons from T4.1 …

6. Listening is also part of communication

- Educating and informing can help improve understanding on particular issues, however on its own it is a very limited strategy and minimizes the values of the process.
- Real engagement requires a two-way flow of information, as it encourages the public to voice their views and interests to inform decisions.

Dunphy N.P., Lennon, B., Quinlivan, L., Velasco Herrejon, P., Curran, R. (2021). Critical review of Education and Public Engagement initiatives. Deliverable 4.1 of the REALISE Horizon 2020 project.

Next steps

- Building on the developed knowledge, an EPE programme will be co-designed with community stakeholders for the Cork Harbour case study.
- The approach will take an intersectional approach, considering the socio-demographic specificities of the relevant communities, *e.g.,* gender, life stage.
- Key elements will be trialed in local communities to evaluate effectiveness, to identify areas of potential improvement, and to ascertain transferability of the programme.

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884266

	Session 2B (chairperson Vesna Middelkoop)
15:00-15:20	Dr. M. Sleczkowski and Dr. Pablo Ortiz - Turning gas separation membranes green with biobased block copolymers
15:20-15:40	Dr. A. Benedito - CARMOF Project: a CO_2 capture demonstrator based on membrane and solid sorbents hybrid process
15:40-16:00	Dr. R.H. Heyn - Introduction to the COZMOS project
16:00-16:20	Dr. L. Petrescu - Converge technology for efficiency methanol production with negative CO_2 emissions: energy and environmental analysis

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Bio-based copolymers for membrane end products for gas separations

BioCoMem

Turning gas separation membranes green with biobased block copolymers

International workshop on CO_2 capture and utilization

TU/e Eindhoven, 16-17th February 2021

Dr. Marcin Ślęczkowski and Assoc. Prof. dr. Katrien Bernaerts

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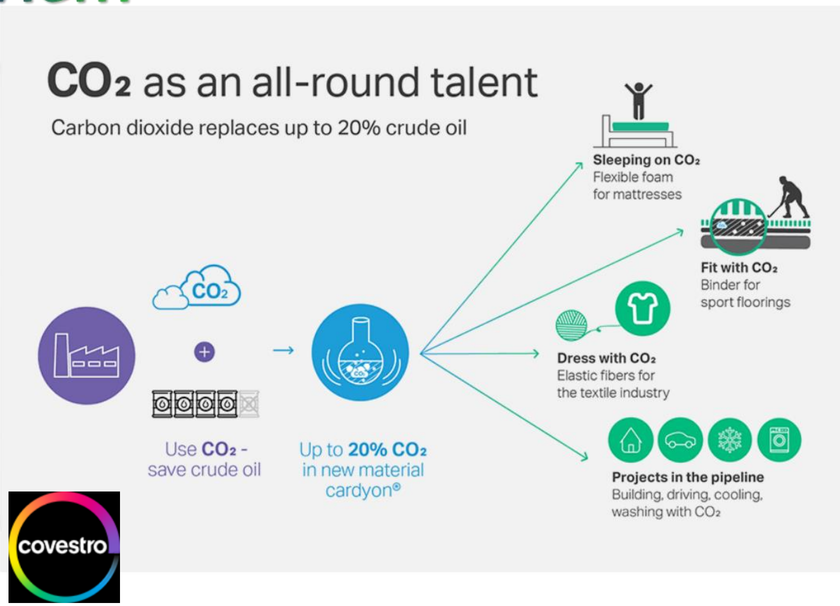
BBI JU

Bio-based Industries Consortium

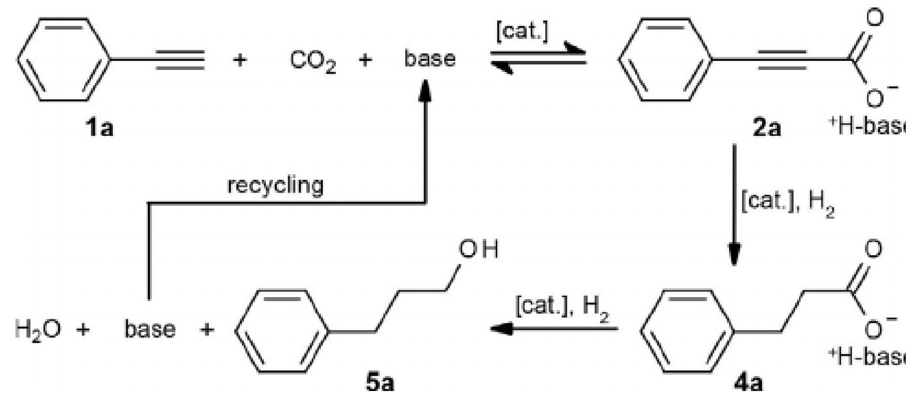
This project has received funding from the Bio Based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme, under grant agreement No 887075.

The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium

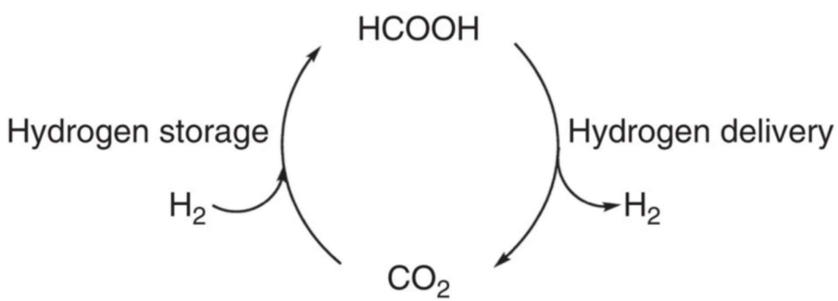
CO_2 recognized as useful raw material.



https://www.covestro.com/en/sustainability/lighthouse-projects/co2-dreams



T. Wendling et al, *Chem. Eur. J.*, 24, **2018**, 6019-6024



S. Moret et al, *Nat Commun.*, 5, **2014**, 4017

De Novo metabolic conversion of electrochemically produced formate into hydrocarbons

eForFuel

www.eforfuel.eu

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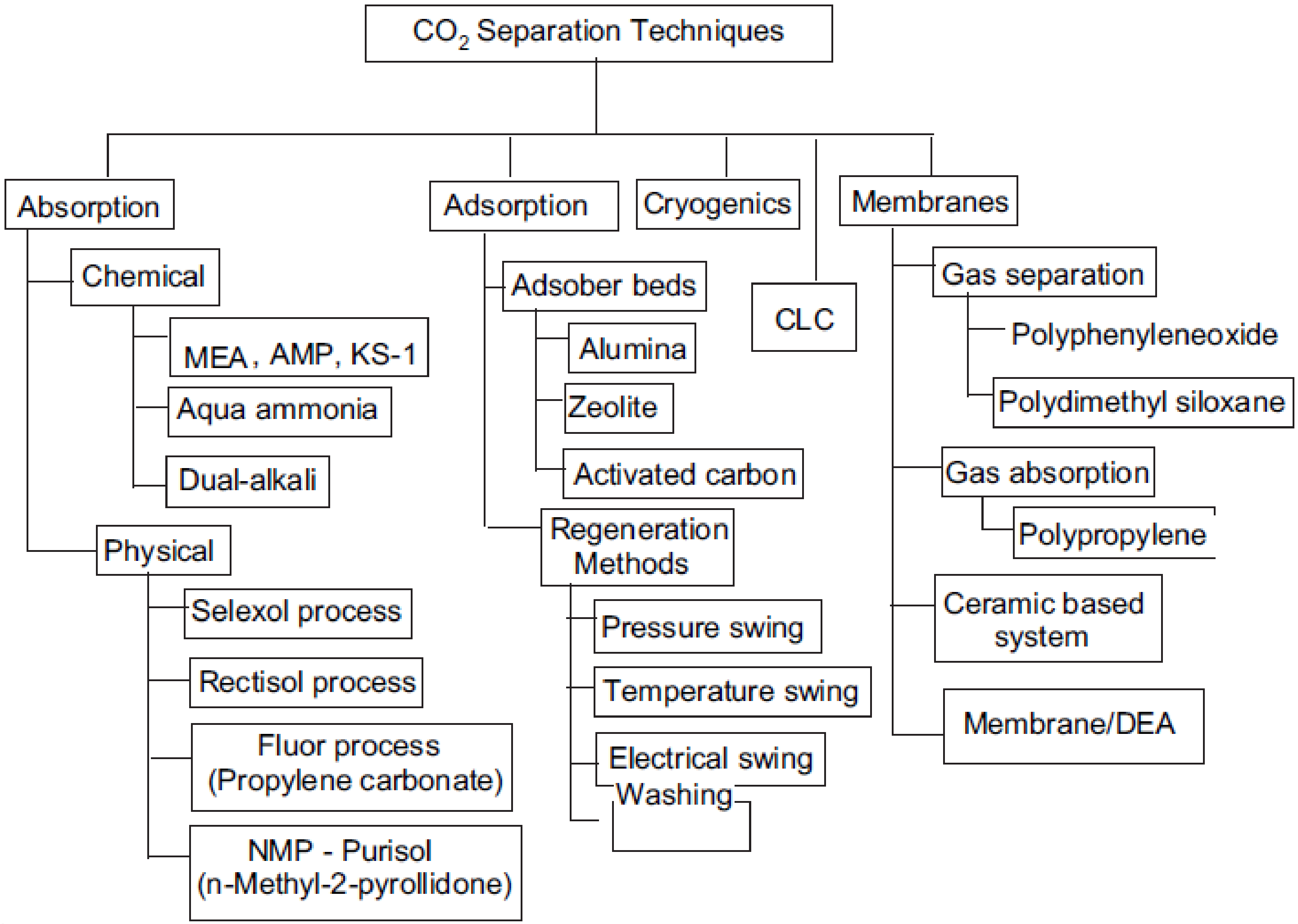
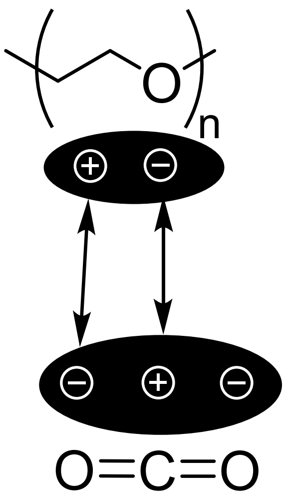
Multiple separation techniques are available.

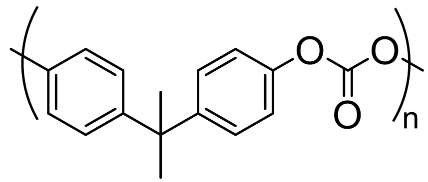


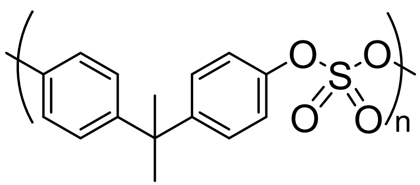
A. A. Olajire, *Energy*, 35, **2010**, 2610-2628

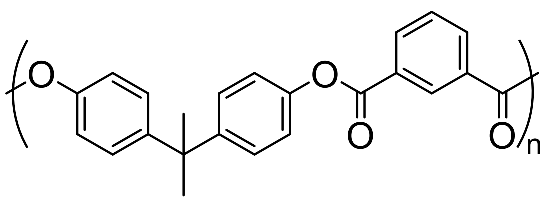
Membranes utilize dipole or ionic interactions

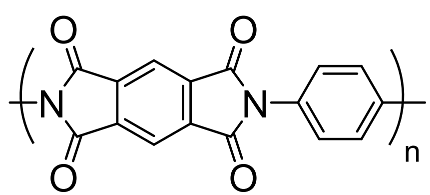
MTR Polaris®
Cross-linked PEO of ~700 g mol^{-1}

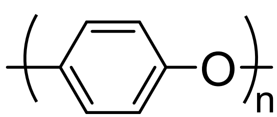




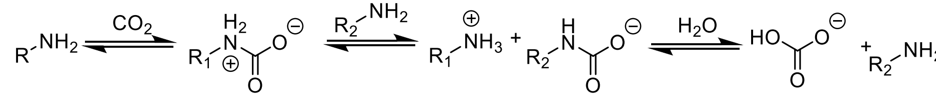




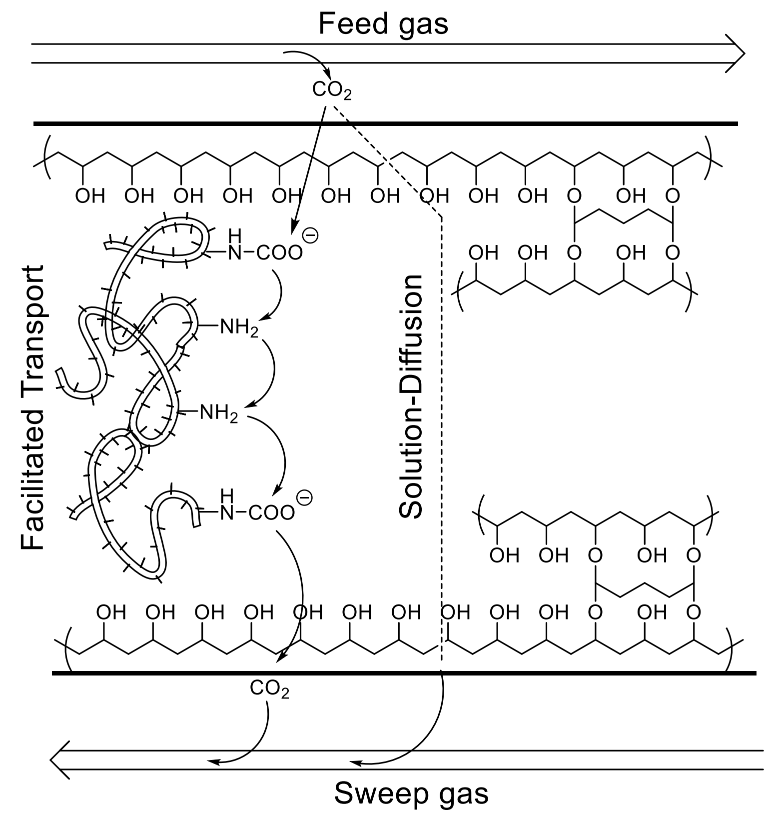


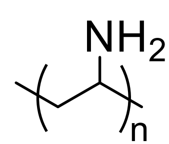


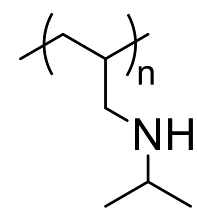
a)



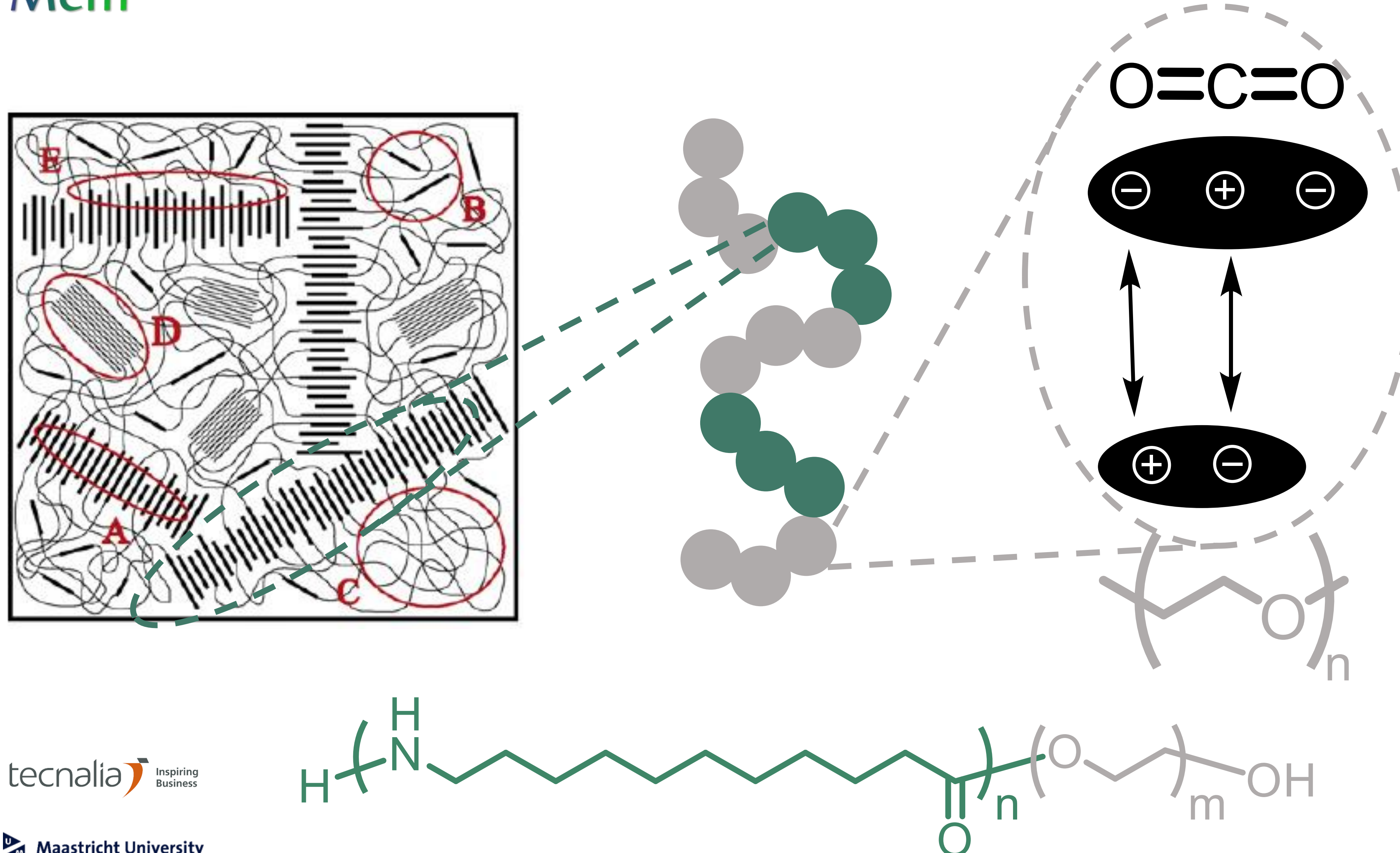
b)







Synergistic effects enhance properties



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Objectives WP3 BioCoMem

Develop bio-based polyether-b-polyamide (PEBA) copolymers as precursors for gas separation membranes at TRL 5, with

- compared to commercially available PEBA PA_{11}-b-PEO
  - higher processability into monolithic hollow fiber membrane (i.e. solubility)
  - higher bio-based content
- additional performance, like
  - higher gas separation performance

  and/or

  - higher resistance to chemical attack (reversible crosslinking)

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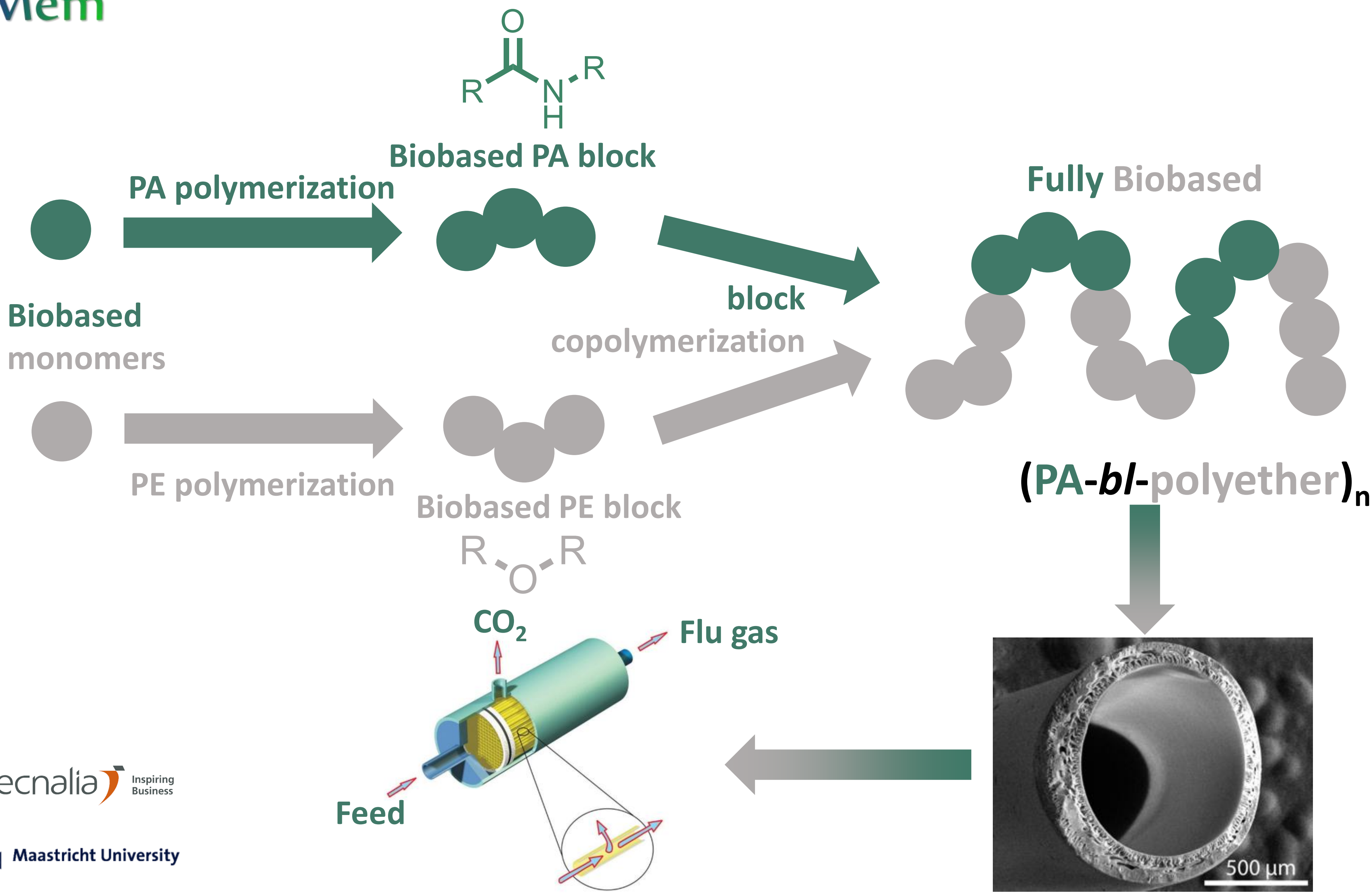
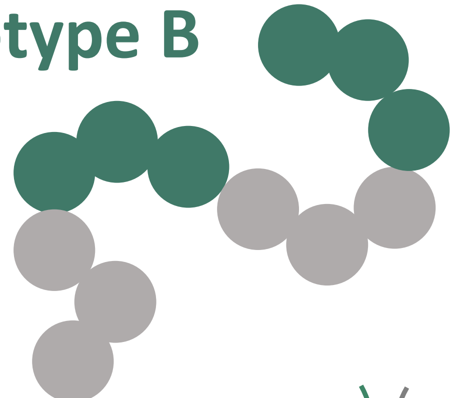
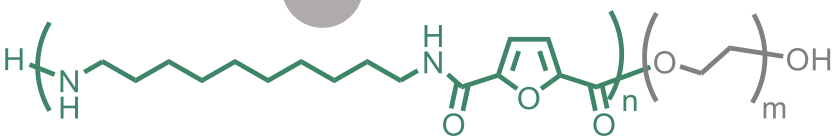
New, biobased block copolymers



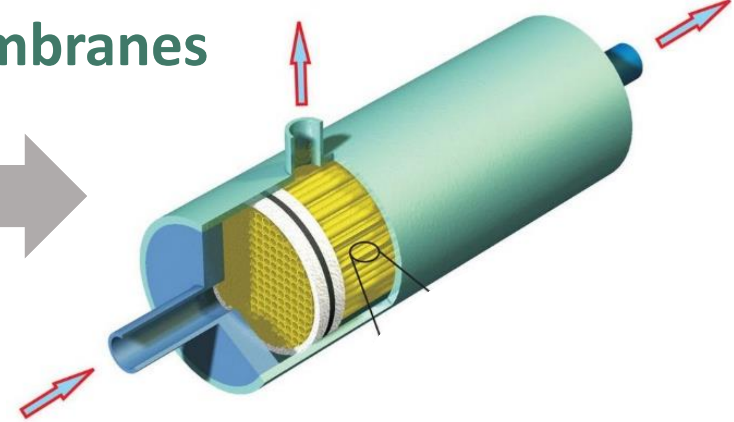
Two new scalable prototypes

Prototype B

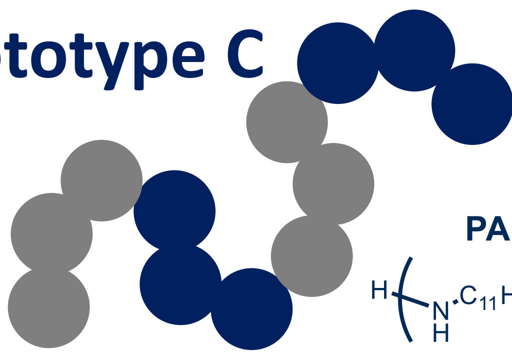


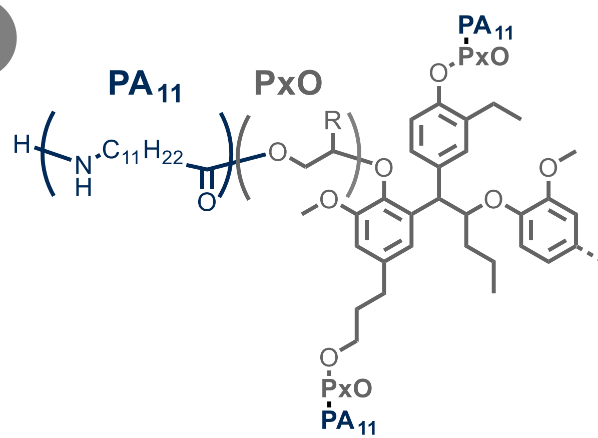


Two new PEBA copolymers suitable for HF membranes



Prototype C





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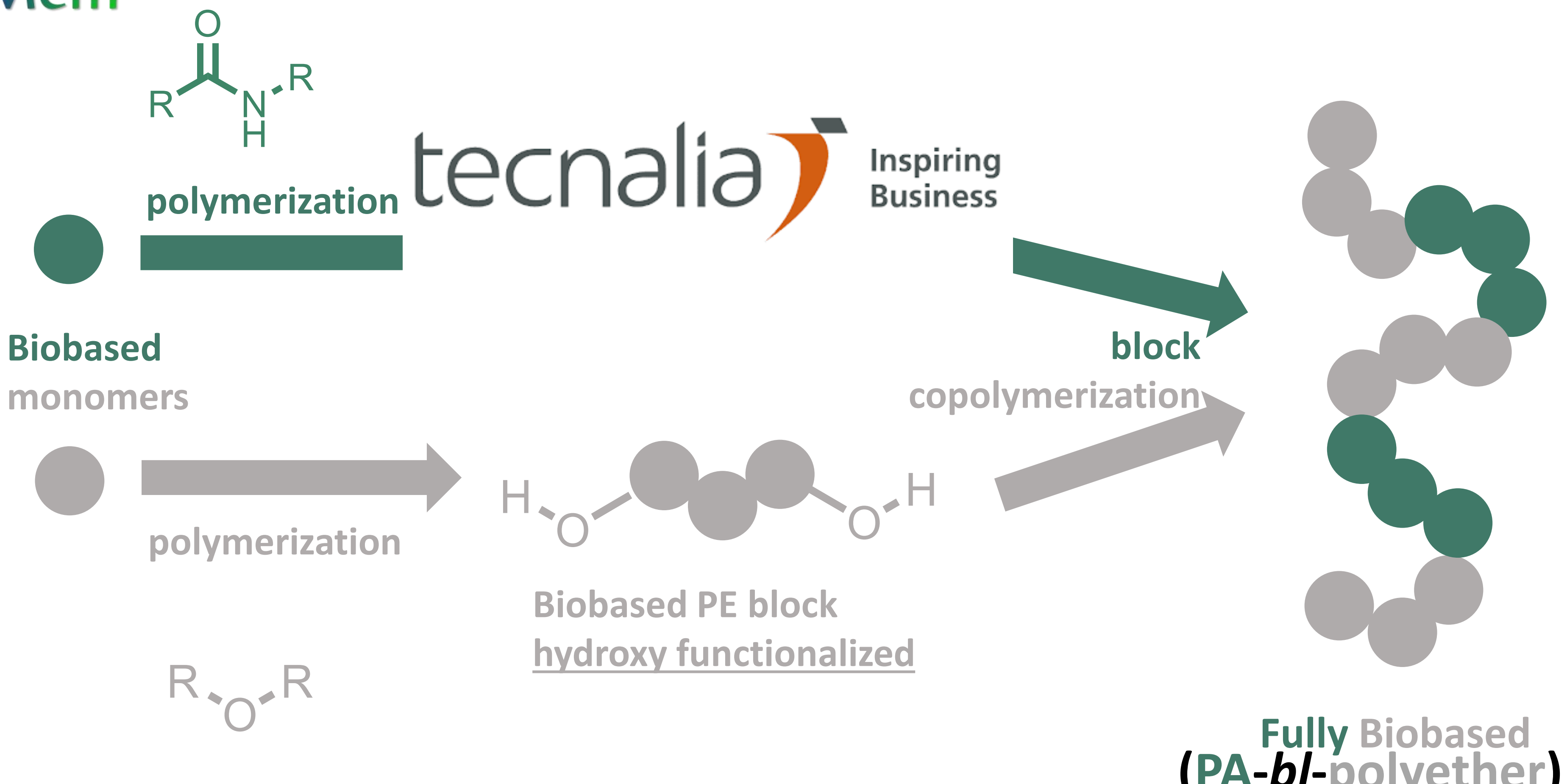
Challenge: synthesis of polymer building blocks



- Synthesis and characterization of both PA and PE blocks
- Synthetic methodology choice / optimization
- Structure – property screening / optimization

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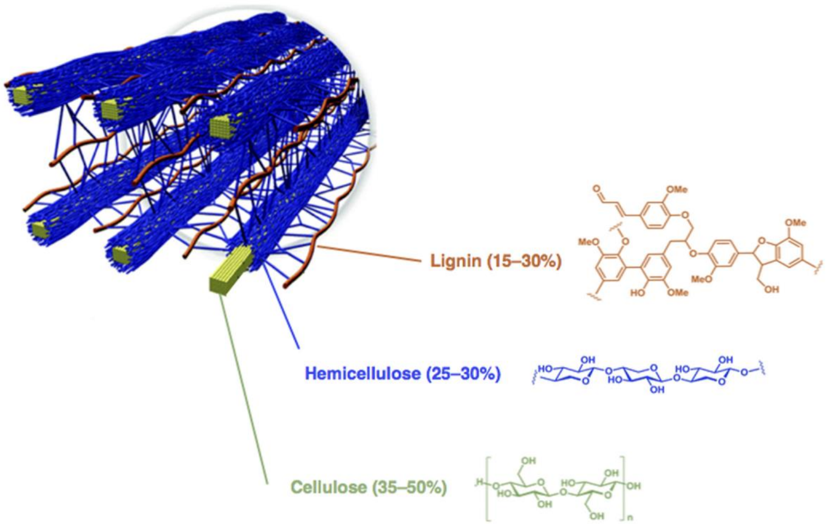
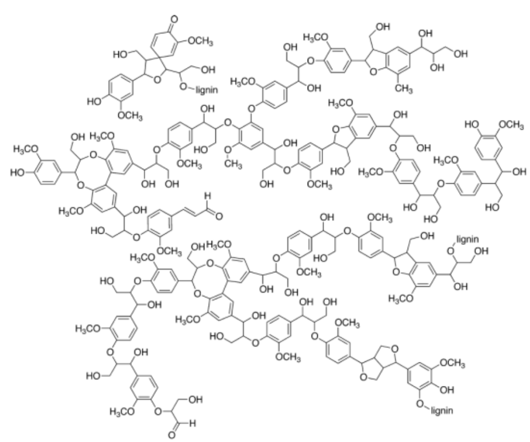
Lignin-based polyols

Lignin overview





Characteristics:

- Availability
- Aromatic content

Currently lignin:

- Low solubility in organic solvents
- Low compatibility with other reagents
- Heterogeneous
- Polydisperse
- Low reactivity

Ways to overcome drawbacks:

- Using mild isolation techniques
- Depolymerizing lignin
- Fractionating lignin (solvent extraction)
- Chemically modifying it

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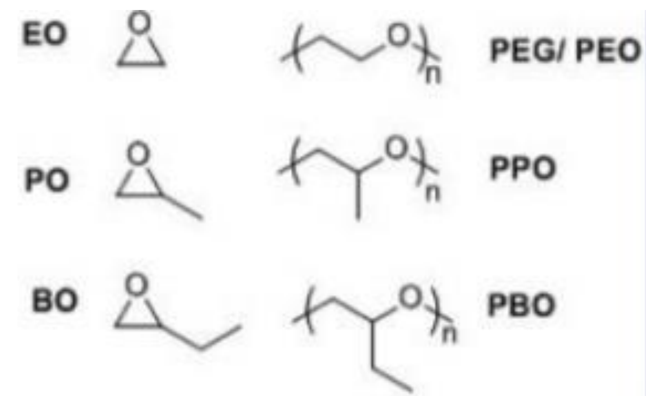
Lignin-based polyols

Anionic ROP of oxiranes



Anionic ROP of oxiranes using lignin as initiator

150-330°C
6-40 bar
Side products
Bad odor

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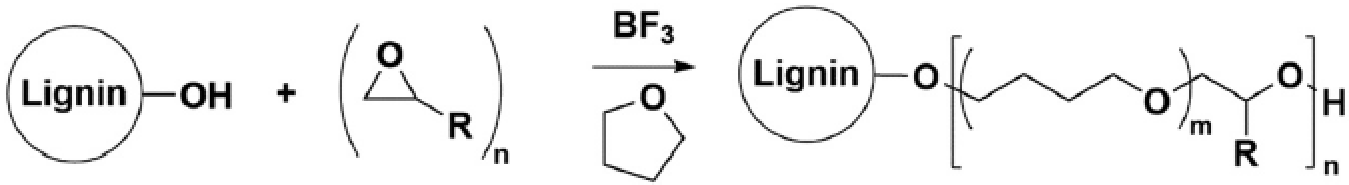
Cellul. Chem. Technol., **2016,** *50*, 941; *Macromol. Mater. Eng.*, **2005,** *290*,1009; *Ind. Eng. Chem. Res.*, **2009**, *48*, 2583

Lignin-based polyols

Cationic ROP of oxiranes using lignin as initiator



WO2020/109460A1; Polym. Chem., 2020, 11, 7362–7369

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Lignin-based polyols

Lignin screening

Mw ≈1000

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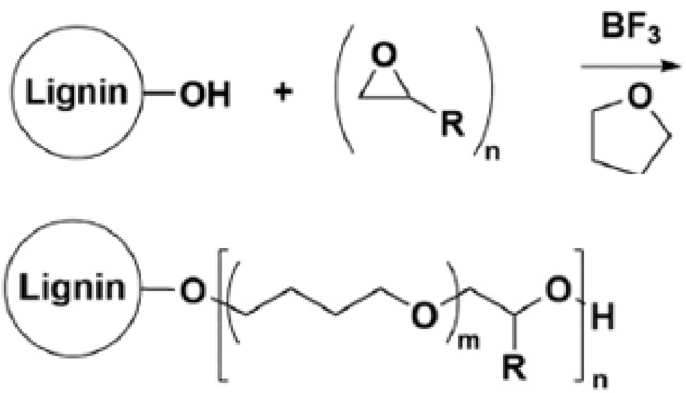
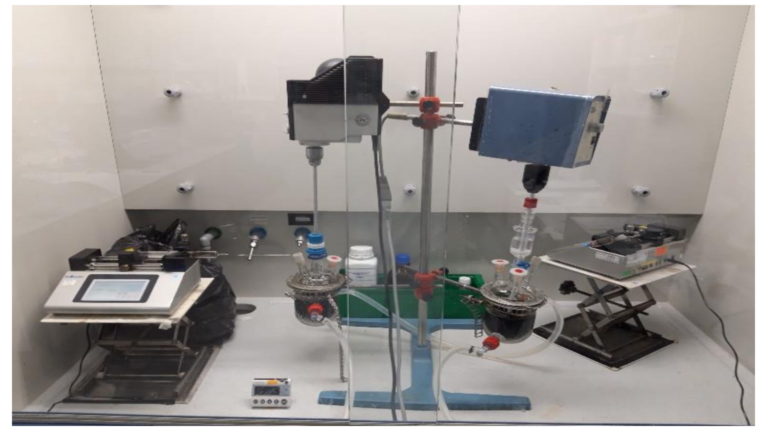
Lignin-based polyols

Initial screening of the reaction conditions





Parameters

- Oxirane
- Concentration of lignin
- Ratio butylene oxide/lignin OH

Results

- Reproducibility
- Viscosity
- Molecular weight
- Polydispersity
- OH number

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Lignin-based polyols

Characteristics

Delivery of 3 LBP to the University of Maastricht

- 3x 50g
- Liquid/viscous
- From 2 different lignins
- M_w: 4000-10000 g/mol
- Lignin content (%): 20-28
- OH number: 86-110 mg KOH/g

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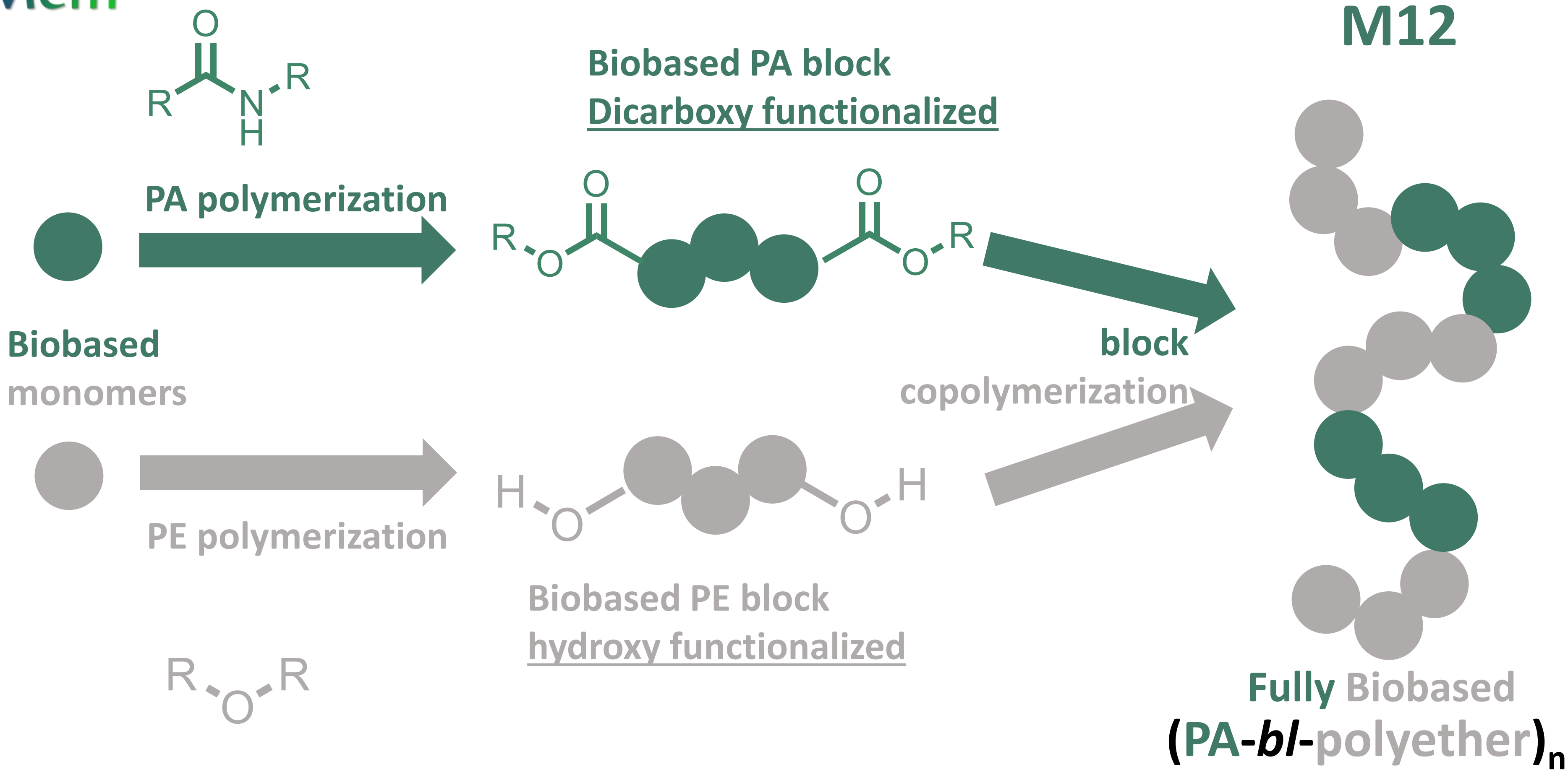
Challenge: synthesis of polymer building blocks

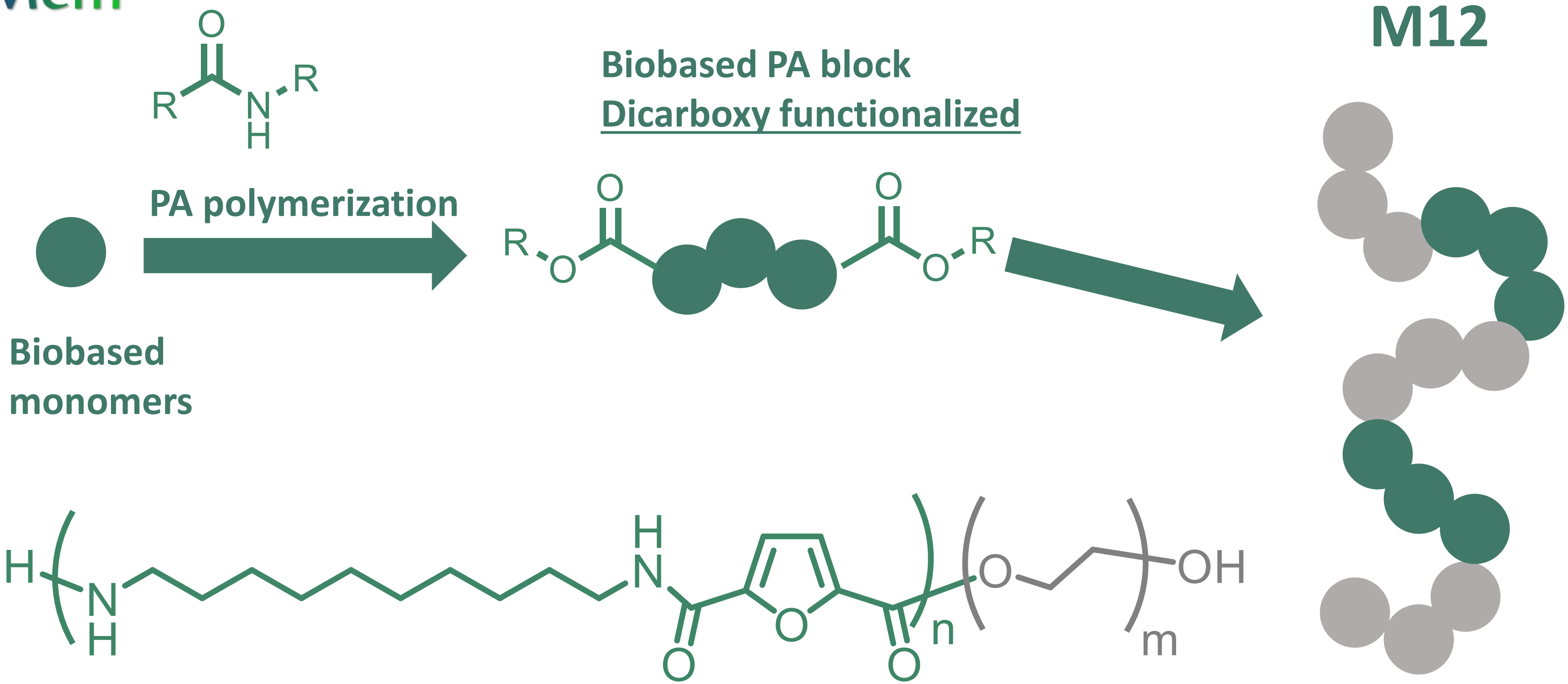
M12



- Synthesis and characterization of both PA and PE blocks
- Synthetic methodology choice / optimization
- Structure – property screening / optimization

Furan-based polyamides for block copolymers

M12



Fully Biobased
(PA-*bl*-polyether)$_n$

- Synthesis and characterization of PA
- Synthetic methodology choice / optimization
- Structure – property screening / optimization

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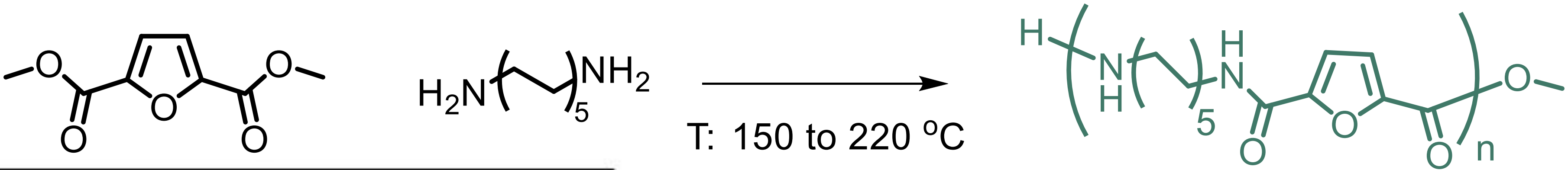
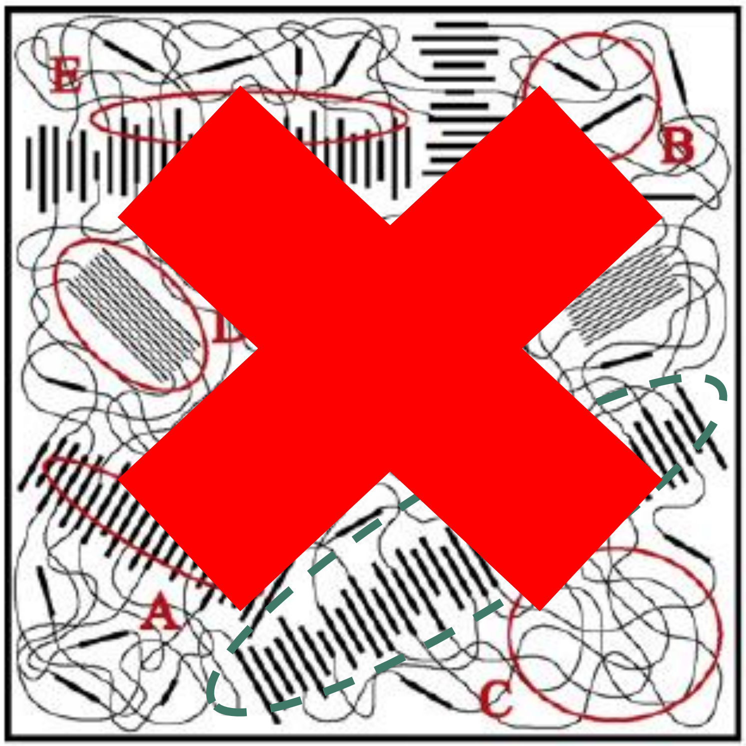
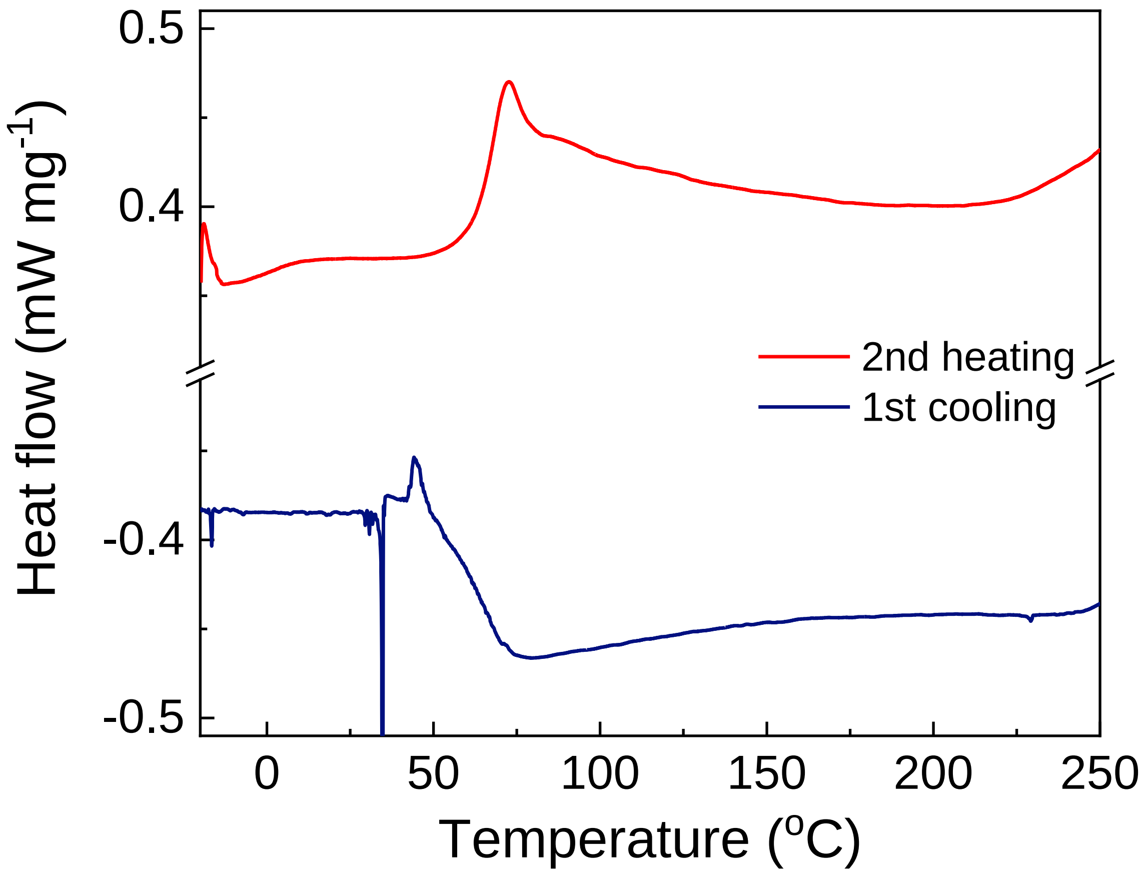
No melting transitions in furan-only polyamide







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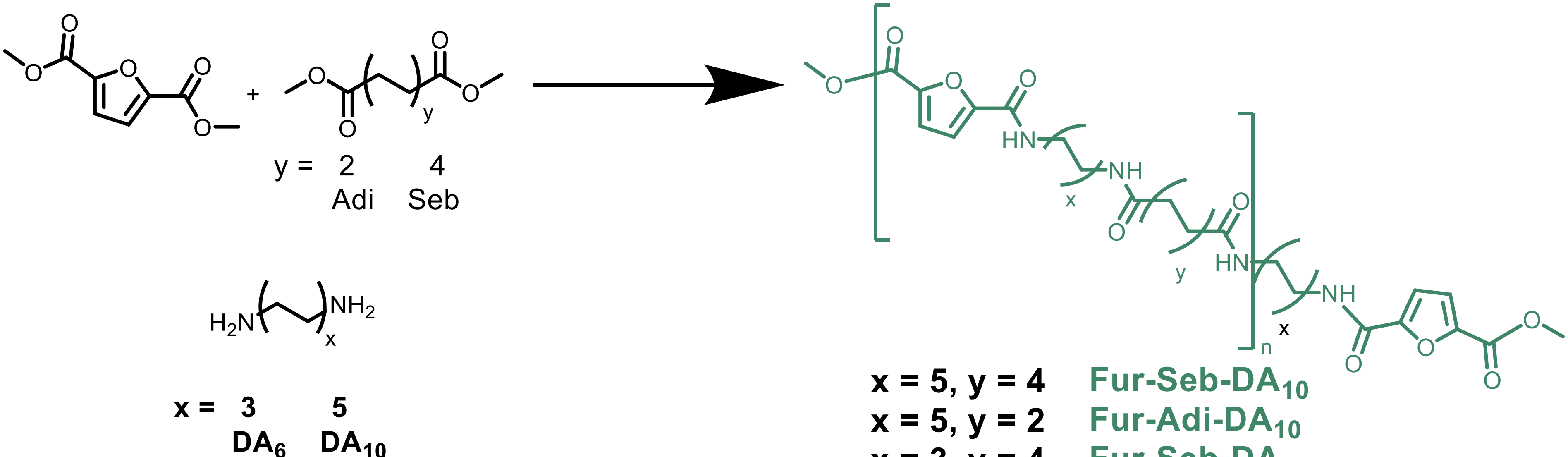
Library of copolyamides with linear comonomers



x = 5, y = 4 **Fur-Seb-DA_{10}**
x = 5, y = 2 **Fur-Adi-DA_{10}**
x = 3, y = 4 **Fur-Seb-DA_6**
x = 3, y = 2 **Fur-Adi-DA_6**

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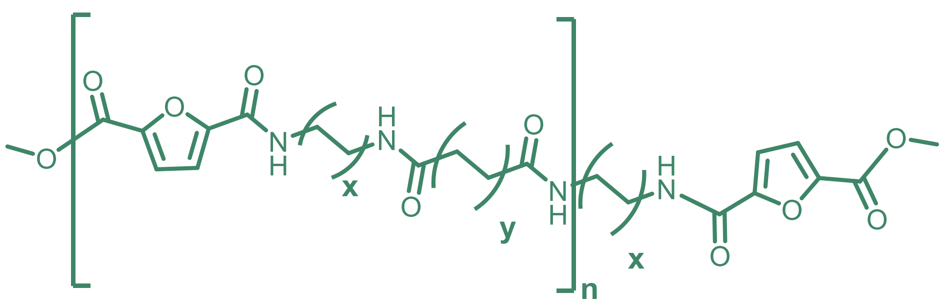
Desired molecular weight and AV are achieved

Feed			Results			
Furan	Sebacate	Adipate	AV	*Calculated M_n [g / mol]*	*M_n (GPC)*	*Đ (GPC)*
1	0	0	92	950		
0.8	0.2	0	112	900	4500	1.8
0.6	0.4	0	93	1000	3500	1.9
0.4	0.6	0	n/a	n/a	2500	2.1
0.2	0.8	0	91	950	2000	2.2
1	0	0	92	950		
0.8	0	0.2	98	950	3000	2.1
0.6	0	0.4	93	950	2000	2.2
0.4	0	0.6	102	1000	3000	2.3
0.2	0	0.8	94	1050	2000	2.4



x = 5, y = 4 Fur-Seb-DA_{10}
x = 5, y = 2 Fur-Adi-DA_{10}
x = 3, y = 4 Fur-Seb-DA_6
x = 3, y = 2 Fur-Adi-DA_6

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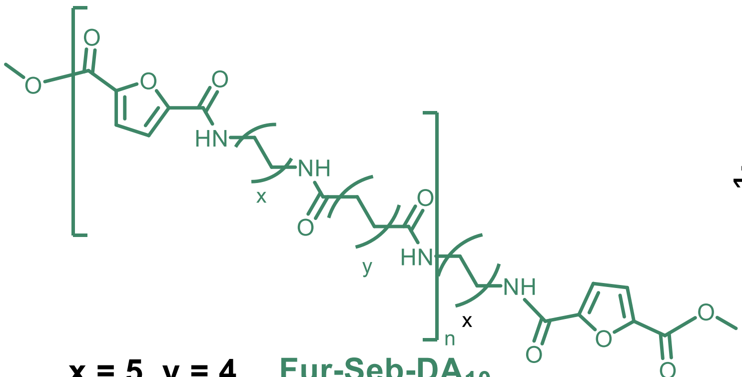
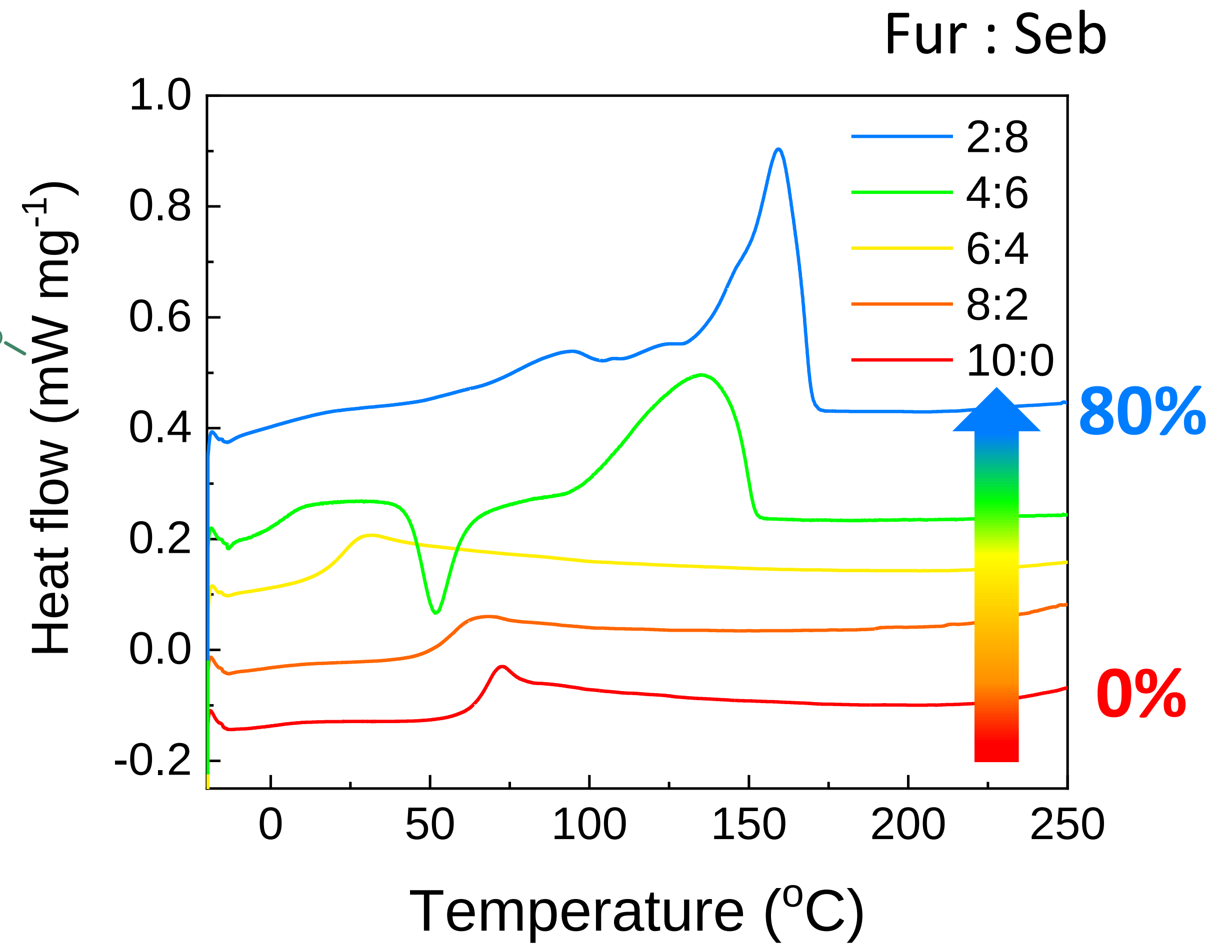
Melting transitions recognized in copolyamides



x = 5, y = 4	**Fur-Seb-DA$_{10}$**
x = 5, y = 2	**Fur-Adi-DA$_{10}$**
x = 3, y = 4	**Fur-Seb-DA$_{6}$**
x = 3, y = 2	**Fur-Adi-DA$_{6}$**

add data for PA11 reference



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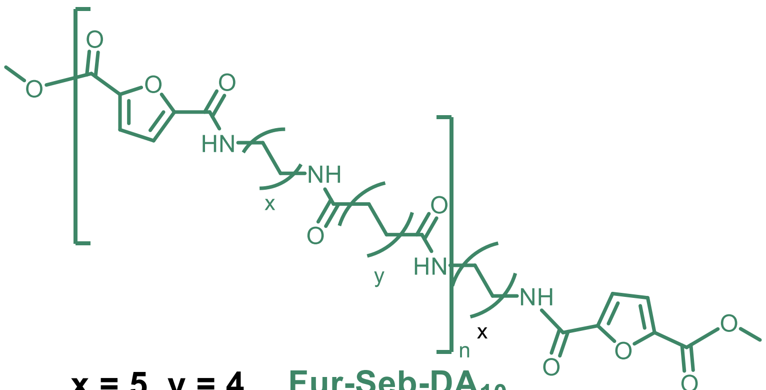
BioCoMem

	Furan	Sebacate	Adipate	T_g [°C]	T_m [°C]
DA10	1	0	0	57	n
	0.8	0.2	0	52	n
	0.6	0.4	0	15	n
	0.4	0.6	0	1	136
	0.2	0.8	0	?	159
	1	0	0	57	n
	0.8	0	0.2	30	n
	0.6	0	0.4	17	149
	0.4	0	0.6	0	168
	0.2	0	0.8	?	218
DA6	1	0	0	90	n
	0.8	0.2	0	43	n
	0.6	0.4	0	36	n
	0.4	0.6	0	9	148
	0.2	0.8	0	?	174
	1	0	0	90	n
	0.8	0	0.2	57	n
	0.6	0	0.4	38	n
	0.4	0	0.6	28	164
	0.2	0	0.8	?	212



x = 5, y = 4 Fur-Seb-DA_{10}
x = 5, y = 2 Fur-Adi-DA_{10}
x = 3, y = 4 Fur-Seb-DA_6
x = 3, y = 2 Fur-Adi-DA_6

add data for PA11 reference

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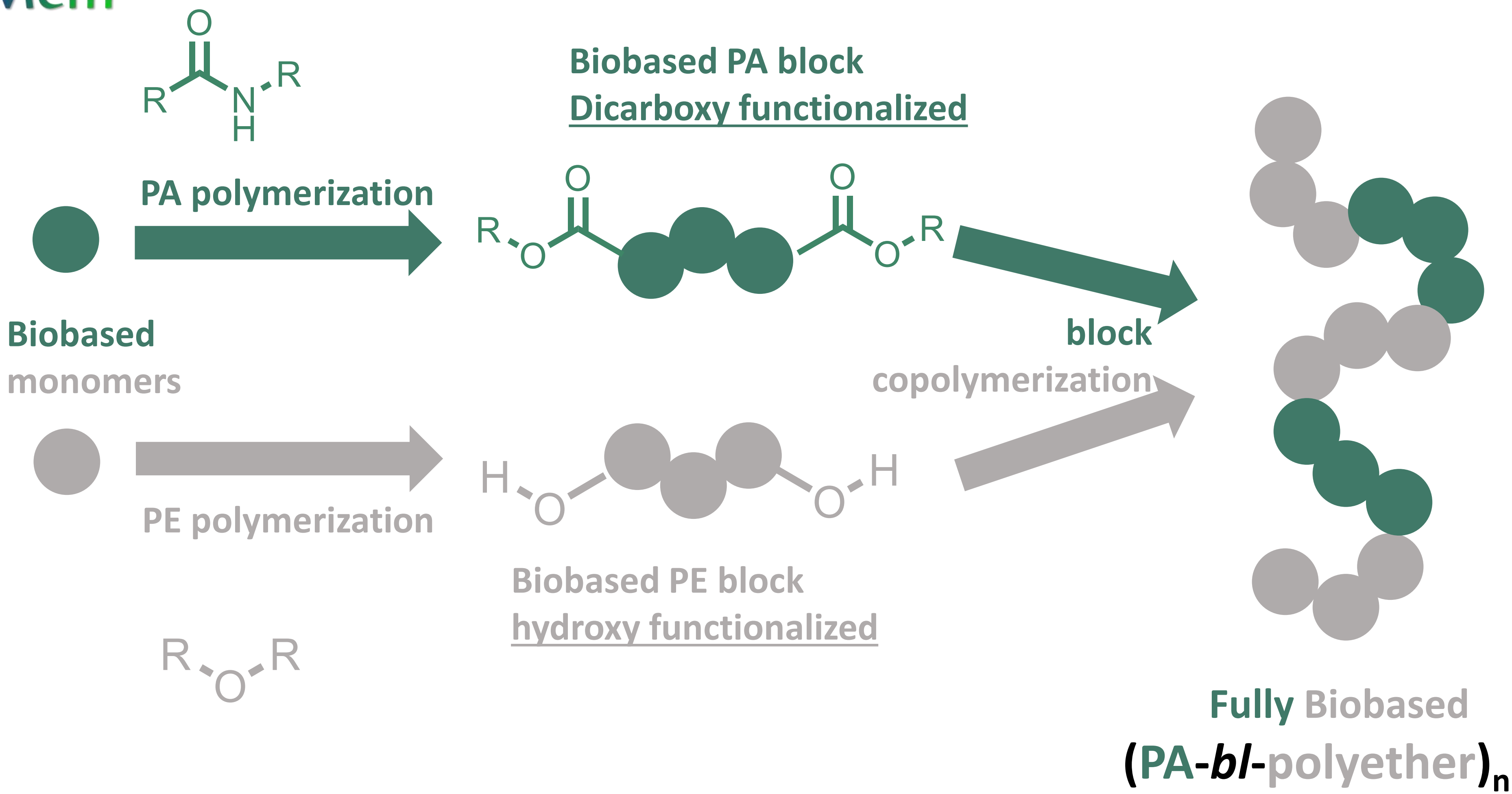
Outlook: synthesis of block copolymers



Bio-based copolymers for membrane end products for gas separations

BioCoMem

Turning gas separation membranes green with biobased block copolymers

International workshop on CO_2 capture and utilization

TU/e Eindhoven, 16-17th February 2021

Dr. Marcin Ślęczkowski and Assoc. Prof. dr. Katrien Bernaerts

m.sleczkowski@maastrichtuniversity.nl
katrien.bernaerts@maastrichtuniversity.nl

Dr. Pablo Ortiz

pablo.ortiz@tecnalia.nl

BBI JU

Bio-based Industries Consortium

This project has received funding from the Bio Based Industries Joint Undertaking (JU) under the European Union's Horizon 2020 research and innovation programme, under grant agreement No 887075.

The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium

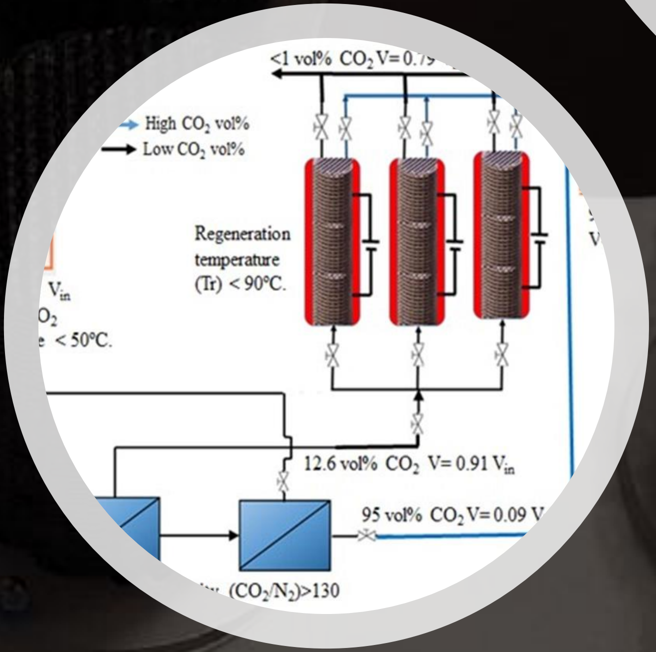
Adolfo Benedito
AIMPLAS
(16&17 February)

New process for efficient CO2 capture by innovative adsorbents based on modified carbon nanotubes and MOF materials.
H2020-NMBP-20-2017

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 760884.
This publication reflects only the author's view and that the Commission is not responsible for any use that may be made of the information it contains.

CARMOF Project

TAILOR-MADE 3D PRINTED STRUCTURES BASED ON CNT AND MOF MATERIALS FOR EFFICIENT CO2 CAPTURE



CARMOF is developing a hybrid CO_2 process combining **VTSA modules** based on 3D printed monoliths with thermoelectric regeneration and "in cascade" **membranes system**. The goal is to achieve high purity CO_2 streams from synergetic effects from both technologies

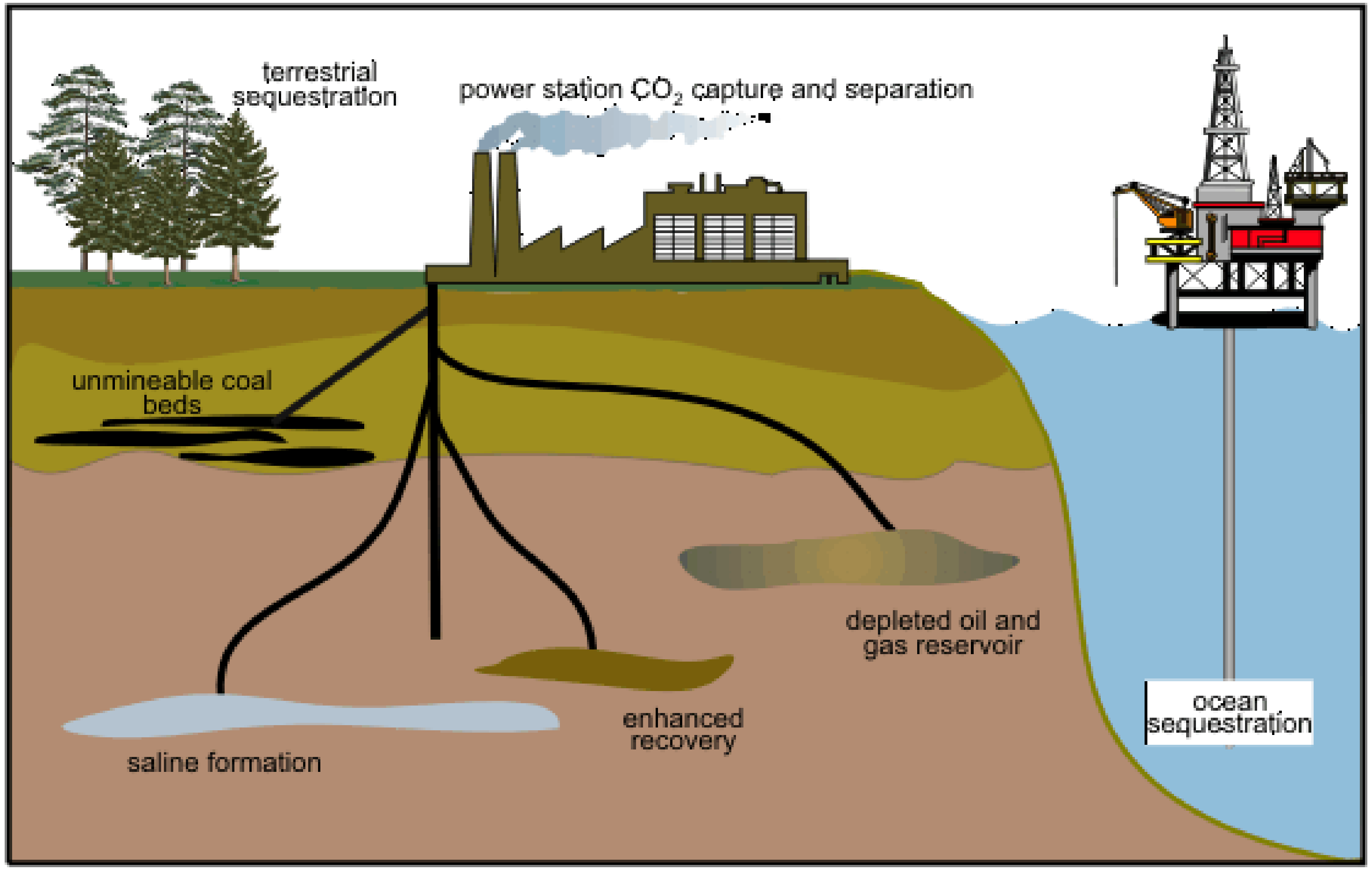
European Commission

CARMOF

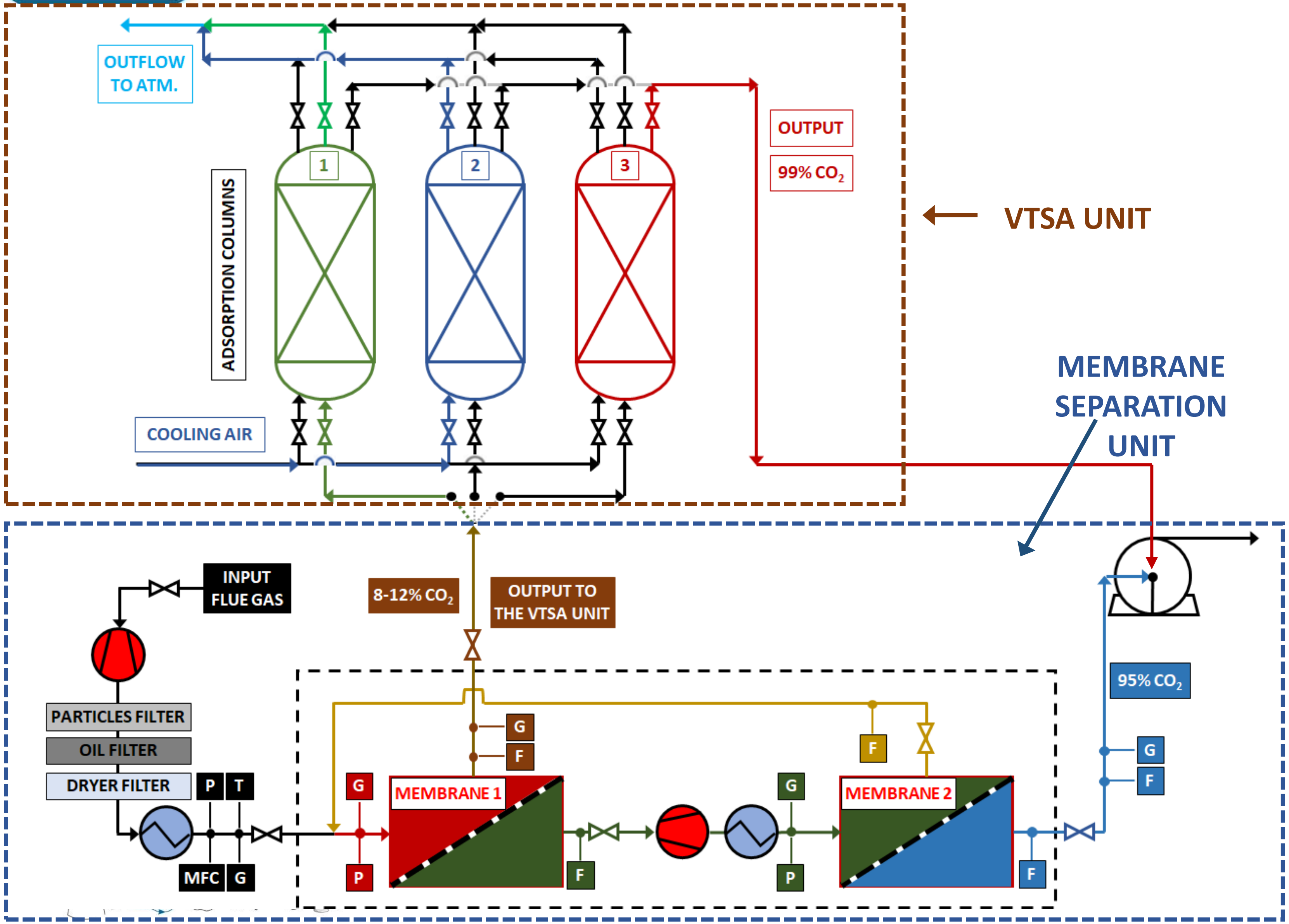
- Consortium consists of 15 partners from 9 countries
- Up to seven industrial pilot plants are proposed across the project – includes both manufacture and capture facilities
- €7.4 M overall budget

Carbon Capture and Storage (CCS)

- Increasing levels of atmospheric CO_2 are a major contributor to anthropogenic climate change
- CCS aims to capture CO_2 from power plants and industry and sequester it underground
- Current capture and separation technologies use organic amines
- Regeneration of these sorbents is inefficient – it can consume up to 30% of the energy produced by a power station!



CARMOF Units



CARMOF is a hybrid system based on:

1. VTSA Unit.
2. Membrane Separation Unit.

Two full ***demo pilot plants*** are planned for 2022 with a capacity of up to 350 tonnes CO2/year.

CARMOF OPPORTUNITY

The **Key Objectives**:

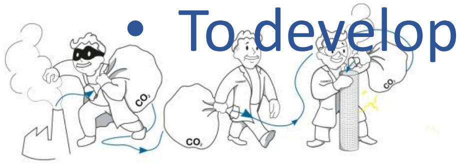
- Industrial scale-up to a **full demonstrator** consisting on hybrid membrane combined with VTSA and Joule Swing (JS) regeneration processes.

- To develop a complete two-stage separation membrane system to couple with VTSA system.

- **Innovative dry sorbents** for post-combustión CO2 capture based on combinations of MOFs, rGO and CNTs, supported by PEI as binder.

- To enhance **manufacturing processes** for these materials combination.

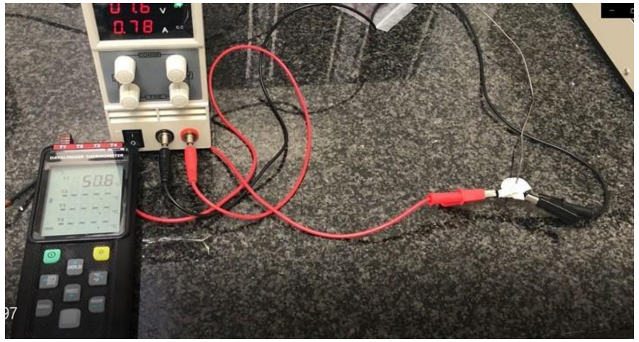
- To develop customized and packed monolith structures based on **3D printing**.

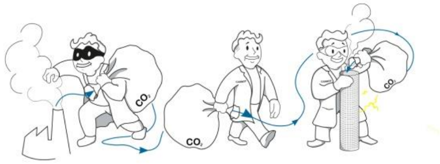


1. VTSA unit

Innovative **dry sorbents**: Production of 3D printed monoliths of porous hybrid nanomaterials for solid phase CO2 absorption.

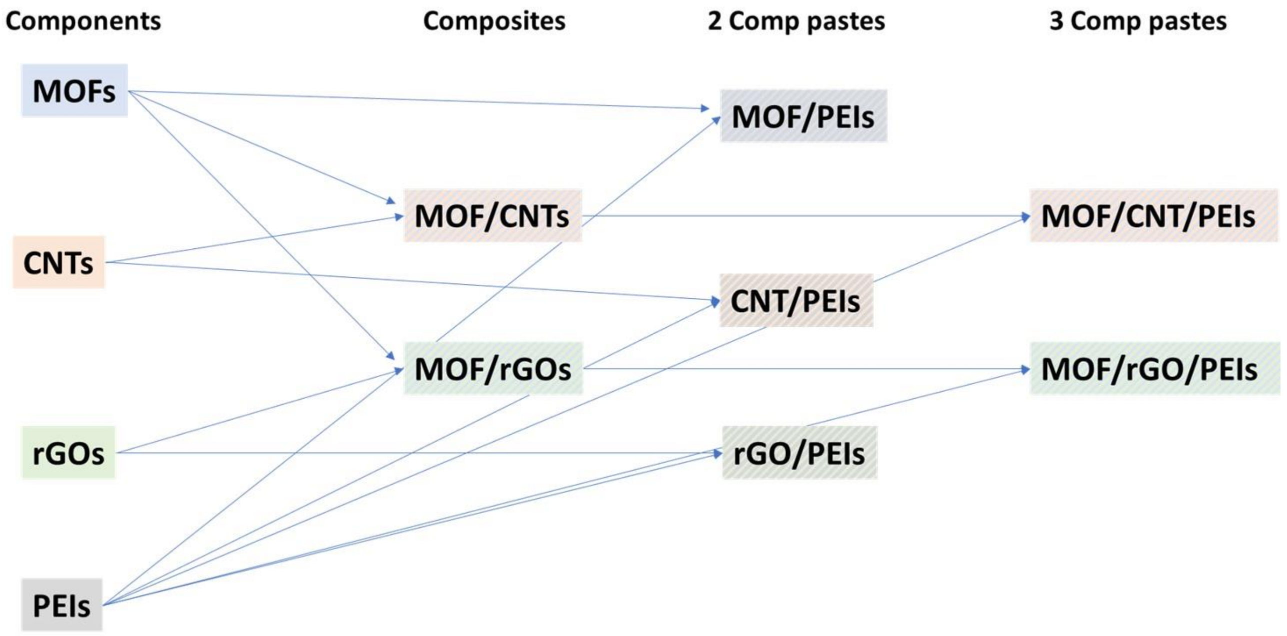
- Hybrid materials based on MOF, carbon nanotubes and reduced graphene oxide.
- 3D printing used to obtain monolithic structures, high packing density and low pressure drop.
- It allows efficient regeneration of saturated sorbents by heating by Joule effect and absorption at vacuum temperature (VTSA).

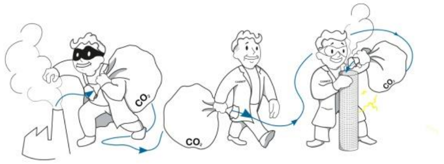




1. VTSA Unit

Innovative **dry sorbents**: Production of 3D printed monoliths of porous hybrid nanomaterials for solid phase CO2 absorption.





- Production optimization and **upscaling of MOF** component.
- Production of **functionalized CNT** component

  MWCNTs, functionalization by oxidation (-OH, -COOH. Etc)
- Production of **functionalized rGO**

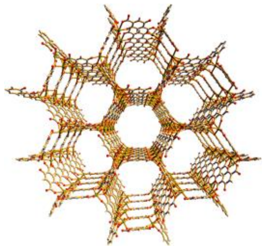
  rGO, carboxylic groups
- MOF/CNT and MOF/rGO **chemical composites**

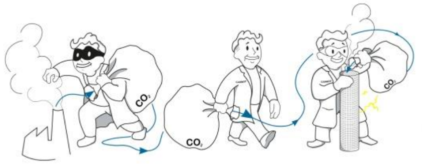
1. VTSA Unit

MOFs for CCS

Requirements:

- High volumetric and gravimetric CO_2 capacity
- High CO_2 selectivity (Power station flue gas is not pure CO_2)
- High chemical and physical stability
- Minimal loss of porosity over many heating/cooling cycles
- Low cost!





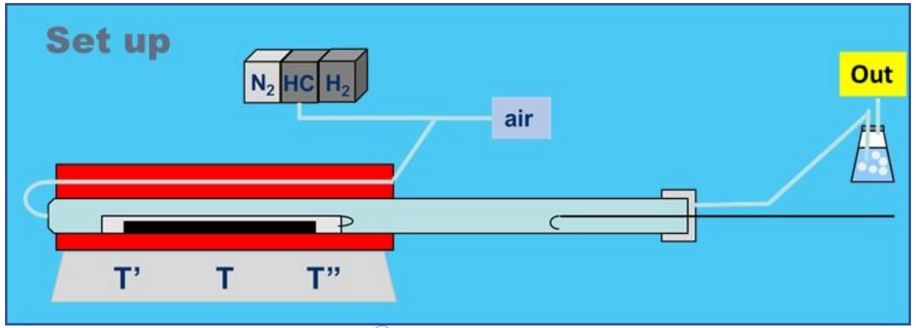
Solution: CPO-27

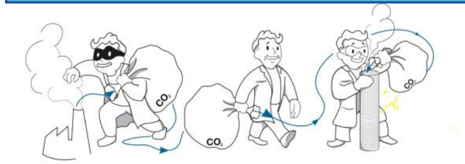
Lab scale reactor system: 100 g MOF/day

Pilot scale reactor system: 5 Kg MOF/day
STY = 266 Kg m^3 day^{-1}

MWCNTs for CCS

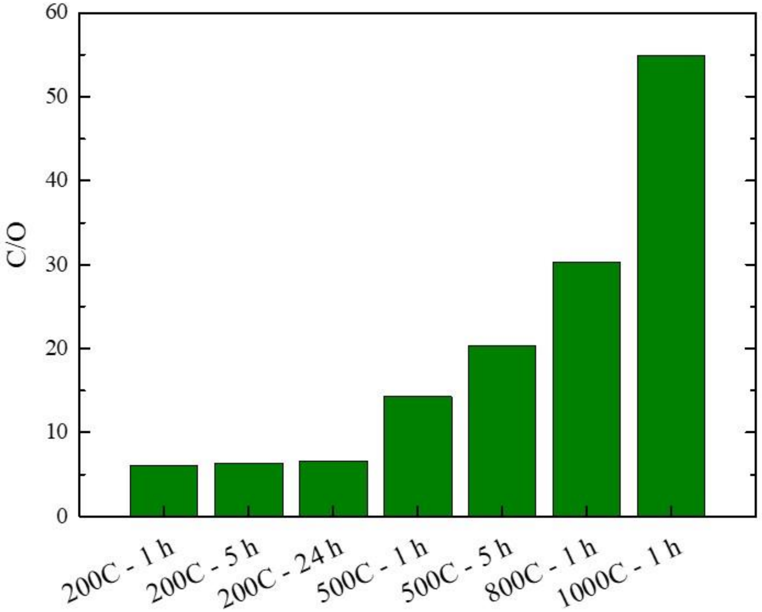
- Oxidation of NC7000 in batch CNT synthesis unit by air/N2 mixtures.
- Effect of temperature, oxidation time, air concentration, gas Flow rate, CNt mass.
- Use of statistical tool: design of experiments.
- Characterization and analysis of results.





rGOs for CCS

Preparation of rGO with different C/O ratios.



Pastes Preparation (Mixing Process)

STEP 1

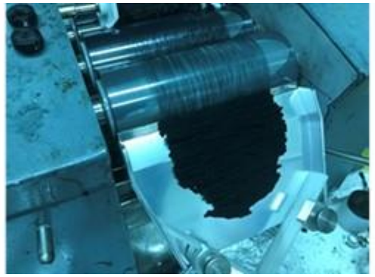
Nanocarbon material

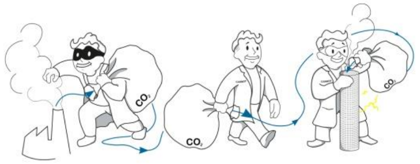
PEI

DISPERSANT AGENT

Manual stirring adding water until obtaining the right texture

STEP 2



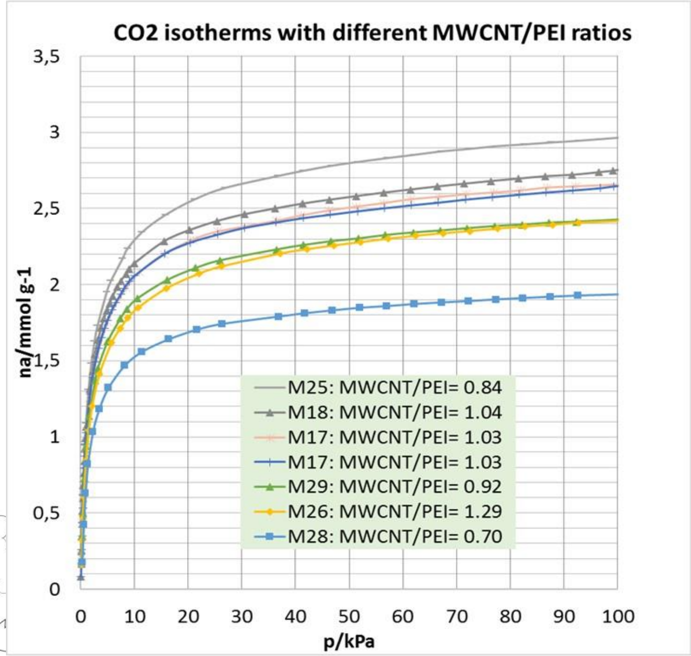


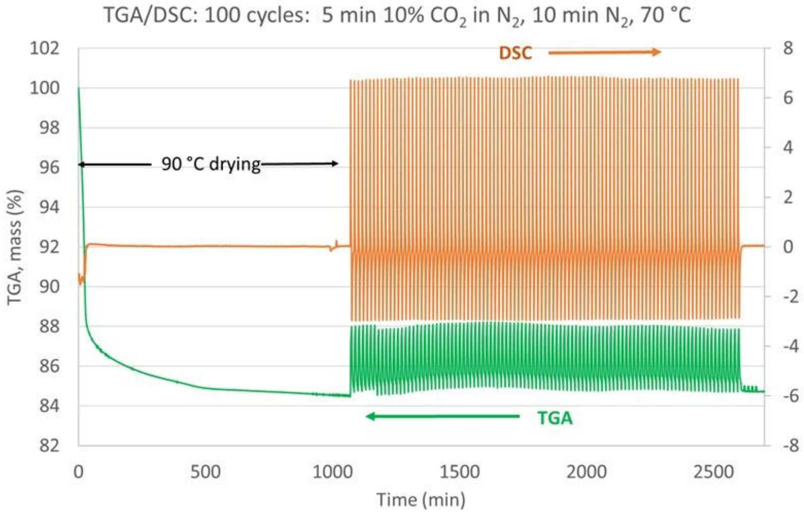
MAIN ISSUES:

- CO2 adsorption values of the material and then after monolith 3D printing process.
- Suitable viscosity for 3D printing.
- To avoid water segregation.
- To control shrinkage through a strong optimization work.
- Homogeneous heating by thermoelectric effect (Joule Effect).

Pastes Preparation (Mixing Process)

Until now best samples are MWCNT/PEI pastes, instead of 3 component. Combinations with rGO are giving promising results.





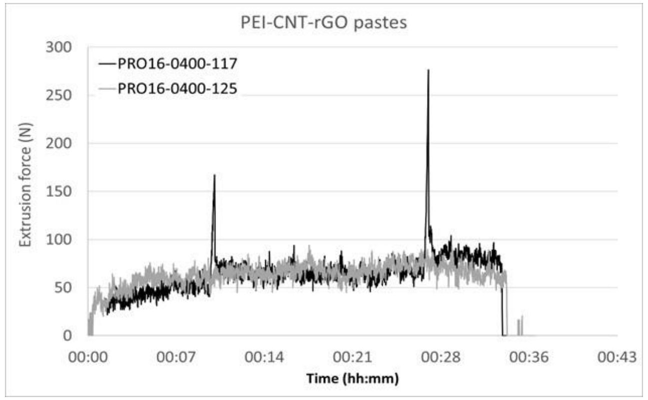
High selectivity to CO2 over other gases as well as stable performance over high number of sorption/desorption cycles.

For the MWCNT/PEI composite, MWCNT may act in two ways:

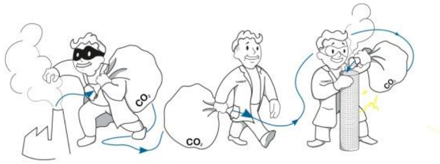
- facilitating the diffusion of CO_2 into the sorbent structure by diffusion through or along its surface, and
- As spacer, avoiding thick aggregates of PEI leading to long diffusion paths through polymeric medium to reach sorption sites.

3D Printing (monoliths)

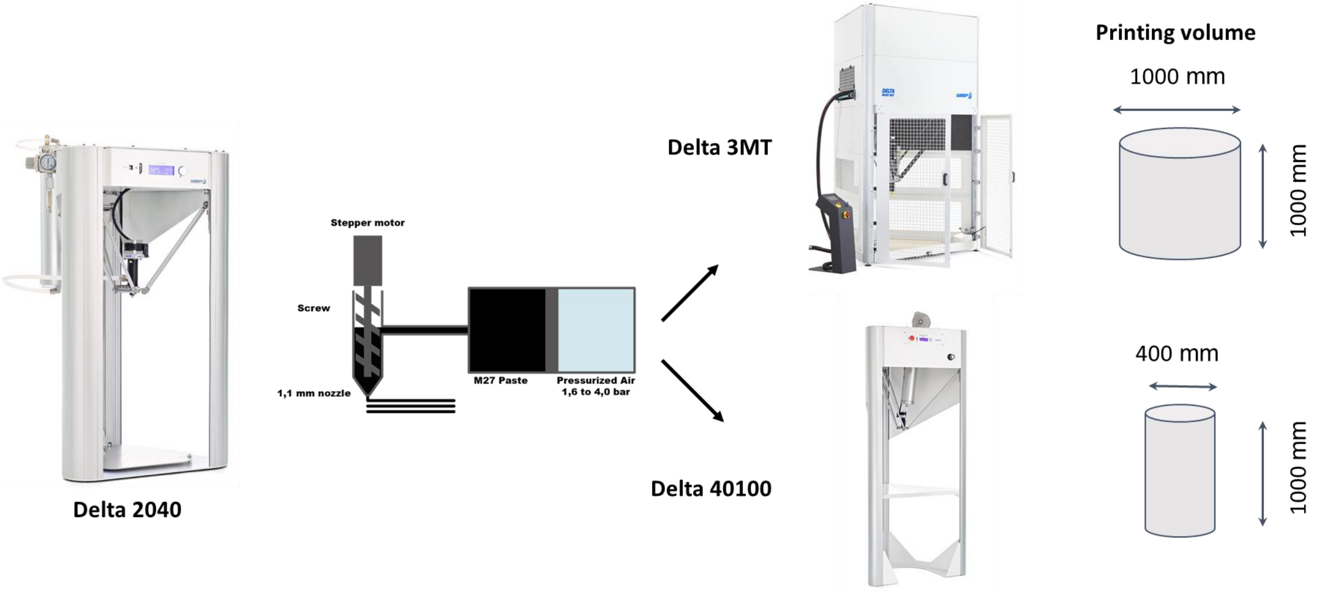
Optimization work related to avoid unstable Flow, phase segregation, bad cohesion of the paste and inhomogeneous shrinkage.

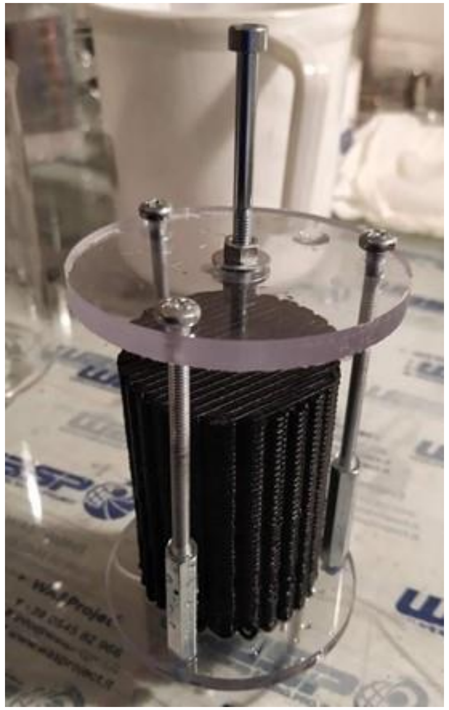


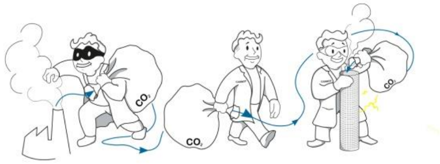
Improvements have been observed with different linkers and dispersing agents. Drop in sorption but to a lesser extent.



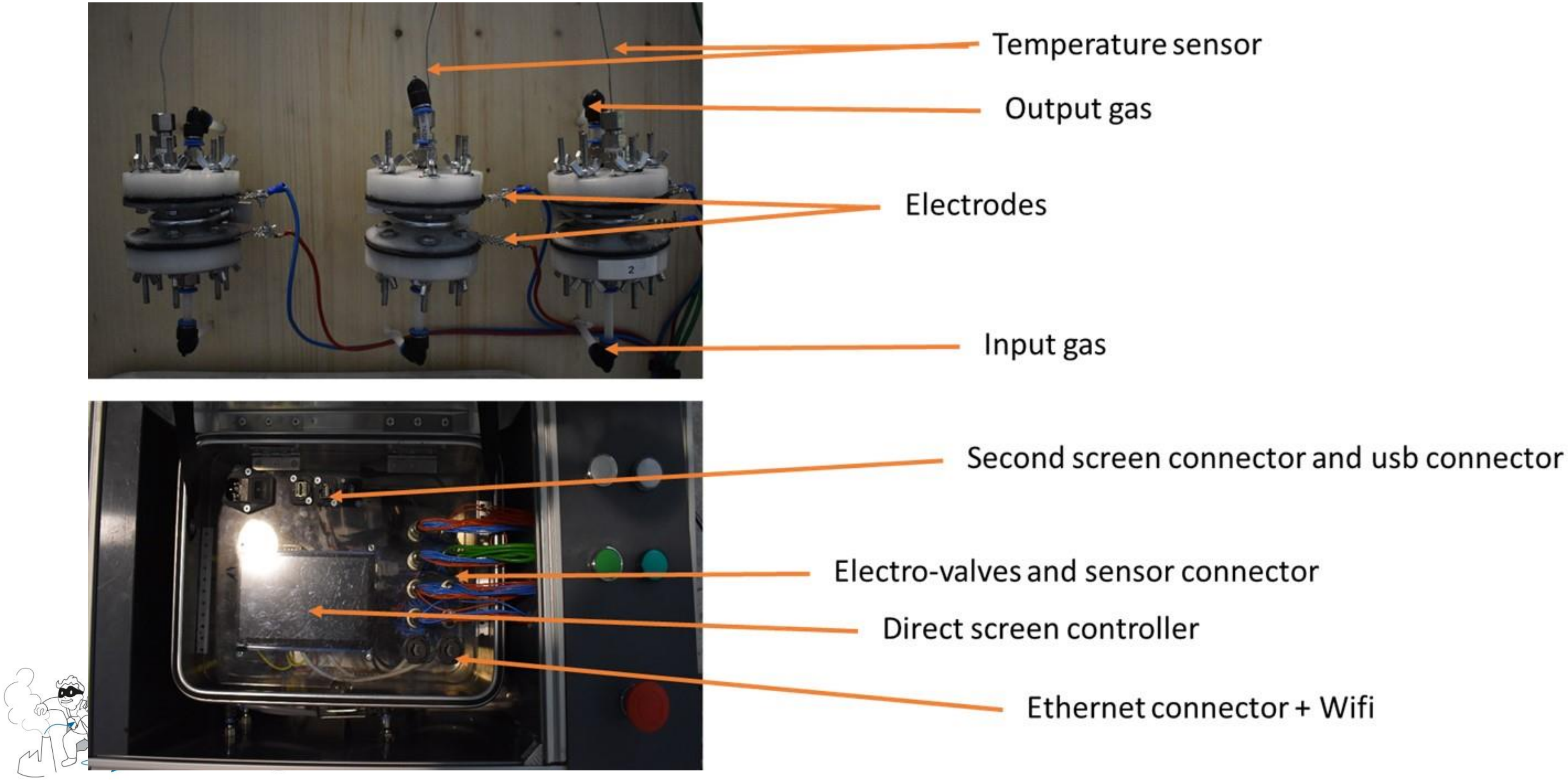
3D Printing (scale-up)





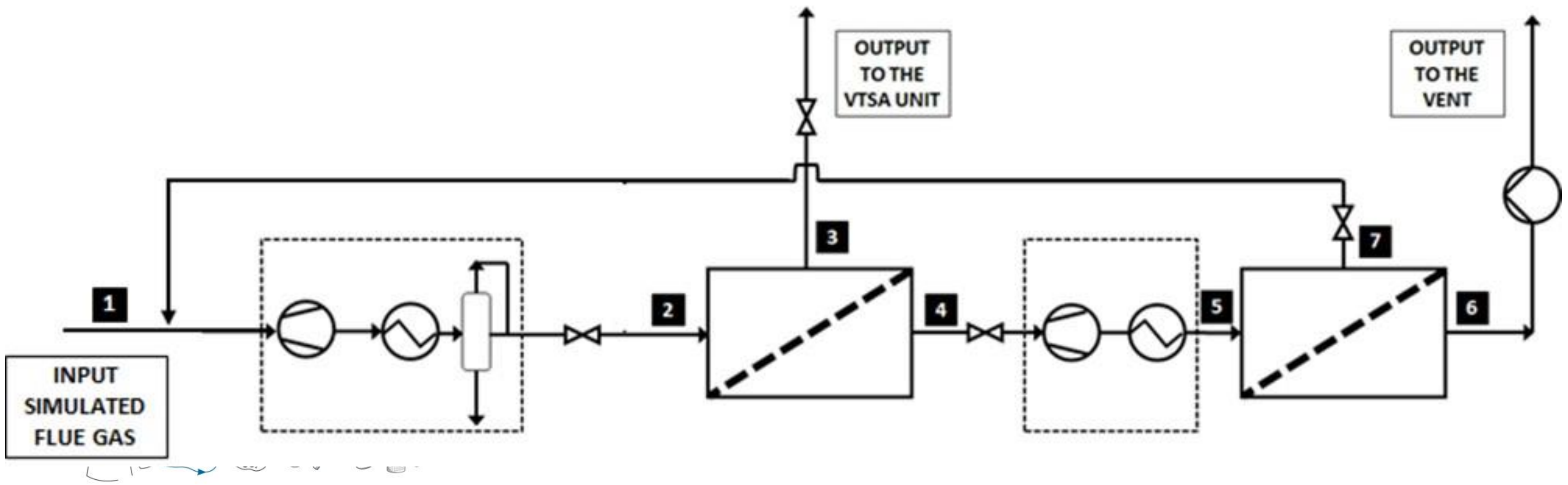


VTSA Benchmark. Joule Effect and sensoring process.



Evaluation of the separation performance of the membrane unit

- Investigation of the effect of **recycling the retentate output of the 2nd membrane module into the gas feed** introduced into the membrane cascade by conducting experimental runs using two commercial membrane modules in series and a dry mixture of 15.6 v/v% CO_2 – 84.4 v/v% N_2 as a feed.



The two-stage membrane section has been tested successfully according to work programme using polyimide commercial membranes

Thank you

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760884.
This publication reflects only the author's view and that the Commission is not responsible for any use that may be made of the information it contains.

Introduction to the COZMOS project

Richard H. Heyn, COZMOS Dissemination and Communication Manager

SINTEF Industry, Oslo, Norway

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

COZMOS - Efficient CO_2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS

- Four year project (01.05.2019 – 30.04.2023)
- Coordinator: Prof. Unni Olsbye, University of Oslo

- Industry partners

- RTO partners

- Foreign partners

Institute for Coal Chemistry (ICC) - China

King Abdullah University of Science and Technology (KAUST) – Saudi Ararbia

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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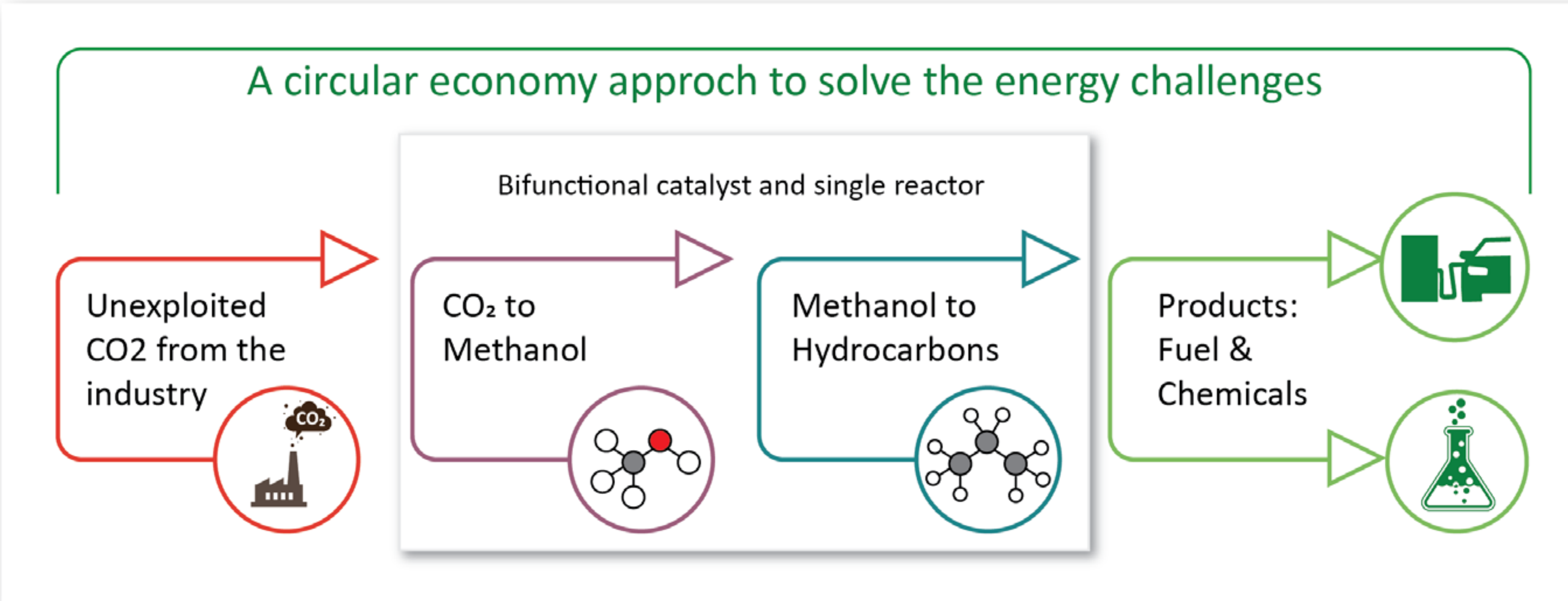
COZMOS in a nutshell



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COZMOS Work Packages

- WP1 – Optimization of catalysts (and process conditions) for cascade reactions
  - Partners: **Univ. Oslo**, Haldor-Topsoe, CNRS, SINTEF, Univ. Torino, ICC, KAUST
- WP2 – Process design and optimization
  - Partners: **Linde**, Haldor-Topsoe, Tata Steel, Tüpraș
- WP3 – Demonstration (TRL5)
  - Partners: **Tüpraș**, Univ. Torino, Tata Steel, Linde, Haldor-Topsoe
- WP4 – LCA, TEA and social aspects
  - Partners: **Tata Steel**, Univ. Sheffield, Tüpraș
- WP5 – Communication, dissemination, outreach and exploitation
  - Partners: **SINTEF**, Tata Steel, Linde, Univ. Sheffield
- WP6 – Ethics
- WP7 – Management

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuel and OlefinS.
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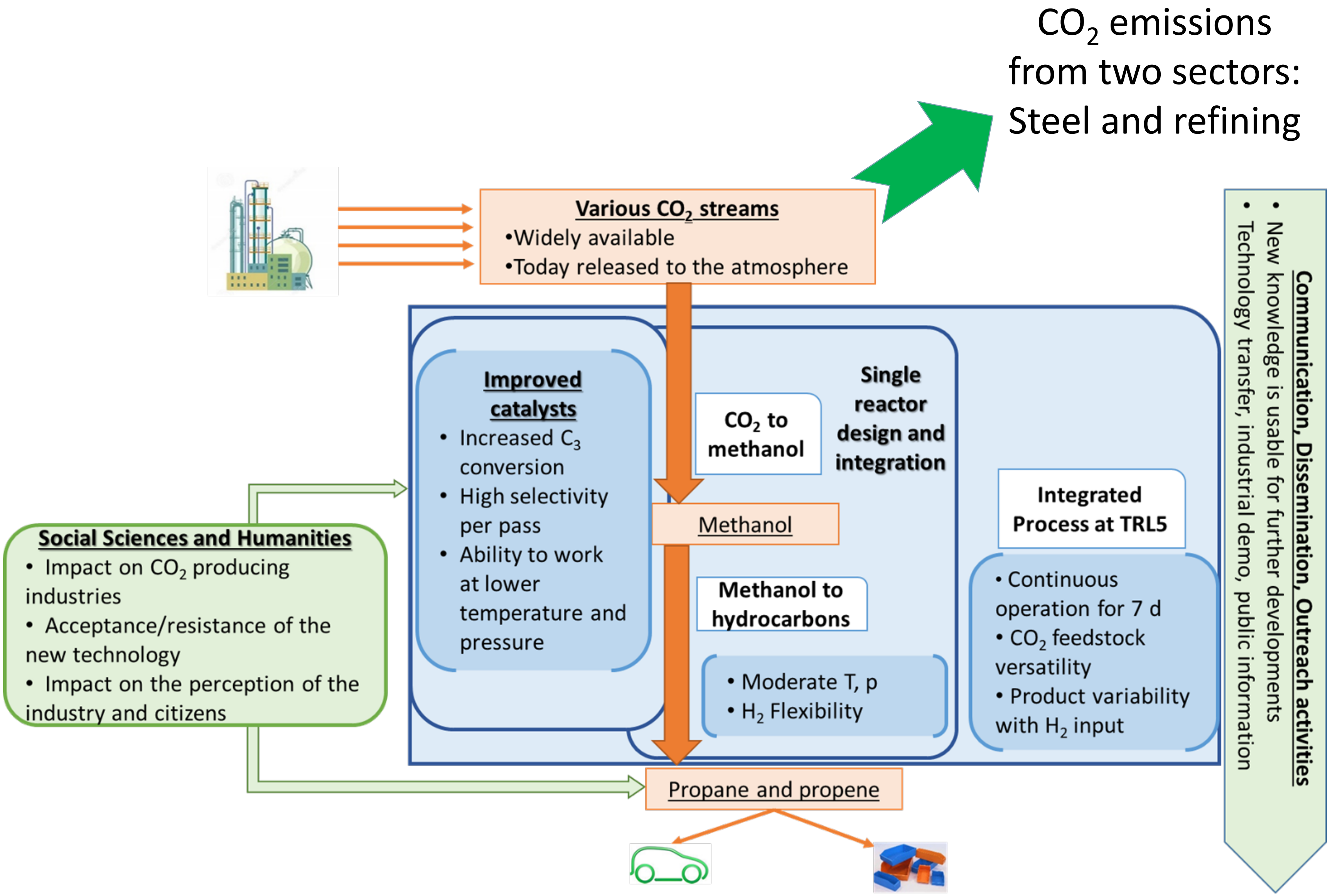
Project overview



COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuel and OlefinS.
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Project Objectives and Innovations

- Development of an energy efficient, economically viable, environmentally friendly and socially acceptable process
- Development, optimization and upscaling of a combined catalyst for hydrogenation of CO_2 to C_3 products
- Determination of optimal process conditions, *i.e.*, optimal heat and pressure management with minimal separation
- Overall integration and validation in a relevant environment (TRL 5)

- Innovation 1: Tailor-made bifunctional catalysts for maximizing the yield, working at low temperature and pressure for both steps, with feeds with various compositions
- Innovation 2: Single reactor and optimized global process design for operation under conditions that are optimal from an energetic and techno-economic perspective, with efficient heat and pressure management, minimized separation and optimized recycling

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuel and OlefinS.
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Impact

- Decrease in CO_2 emissions by 1.9 t_{CO2} / $t_{C3\ product}$
    - DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V., *Low carbon energy and feedstock for the European chemical industry*, 2017
- Convert 0.4 Mt CO_2/yr in 2030, 2.2 Mt CO_2/yr from 2034
- Flexible solutions for local requirements and different industries.

- Key aspect is availability of H_2
    - Must be made from renewable energies with no (appreciable) carbon footprint

- Scenario 1 – Lots of renewable energy and CO_2, but remotely located
    - Utilize excess renewable energy and make propane, which is a transportable energy vector (heating, cooking, transport)
- Scenario 2 – Limited renewable energy/high demand for H_2, located within established process industry infrastructure
    - Synthesize propene for use within the chemical industry

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuel and OlefinS.
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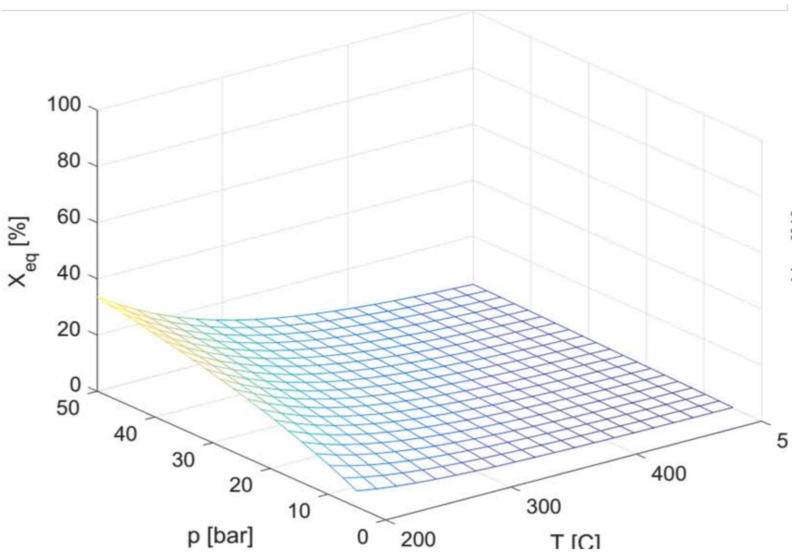
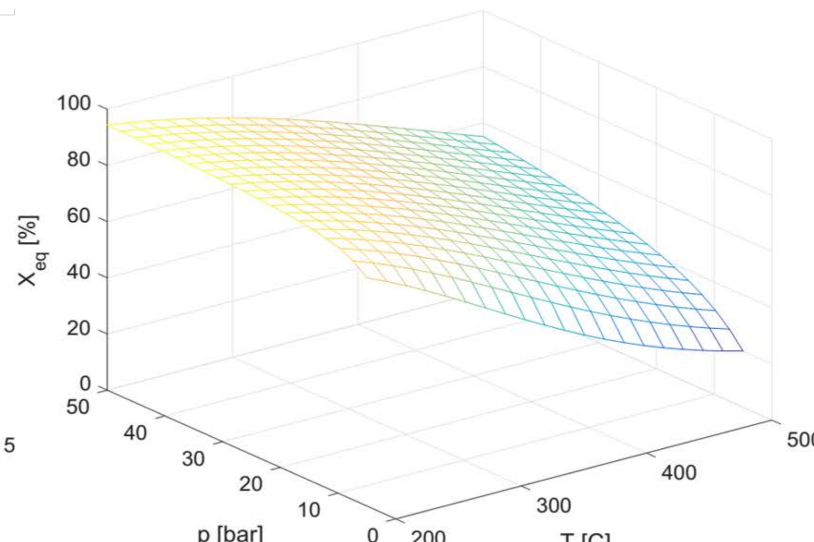
Thermodynamics – Le Chatelier is our friend

- All CO_2 chemistry has thermodynamic limitations
  - Hydrogenation of CO_2 to MeOH included
- If a second reaction converting MeOH is combined with CO_2 hydrogenation, CO_2 conversion should increase





Maximum achievable per-pass (equilibrium) conversion of CO_2 to C_3 products
***Left:* Convential two-reactor system. *Right: COZMOS* one-reactor process**

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuel and OlefinS.
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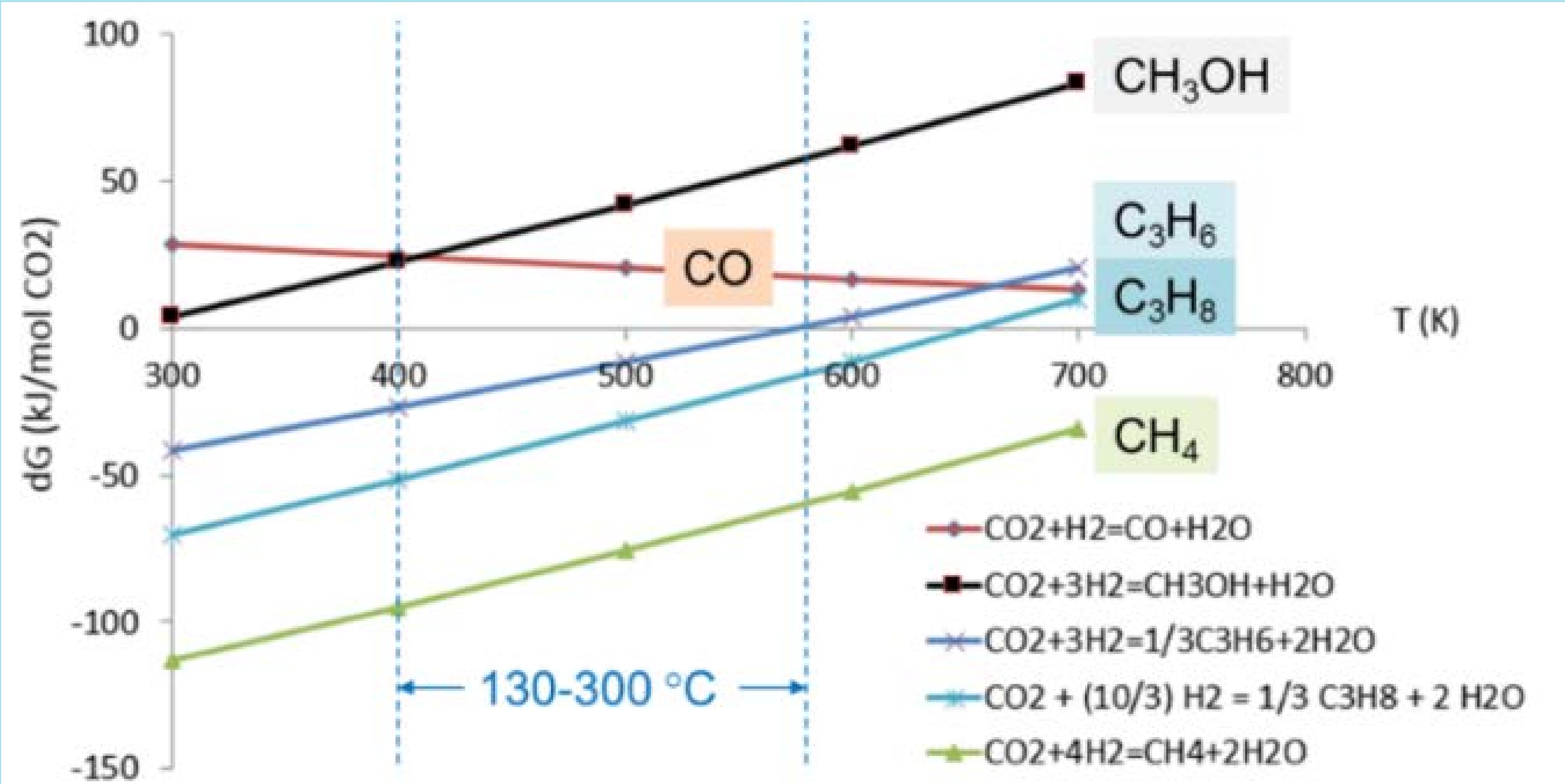
Thermodynamics is our favor



Gibbs free energy vs. Temperature for CO_2 hydrogenation reactions

- Hydrogenation of CO_2 to C_3 products is thermodynamically favorable in a readily accessible temperature/pressure window

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuel and OlefinS.
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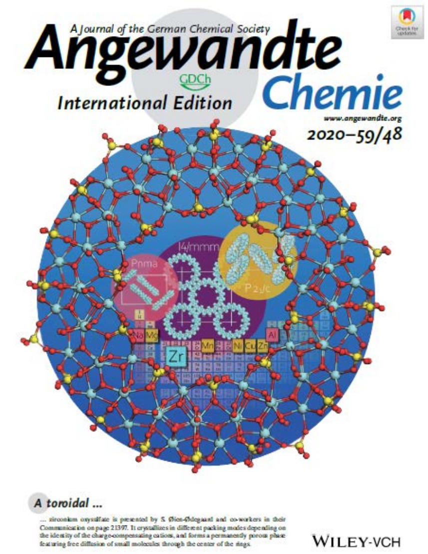
Publications thus far

- On the conversion of CO_2 to value added products over composite PdZn and H-ZSM-5 catalysts: excess Zn over Pd, a compromise or a penalty?
  - From Univ. Oslo, Univ. Torino, CNRS
  - *Catal. Sci. Technol.* **2020**, *10*, 4373-4385
- A toroidal Zr70 oxysulfate cluster and its diverse packing structures
  - From Univ. Oslo
  - *Angew. Chem. Int. Ed* **2020**, *48*, 21397–21402



- Selective Conversion of CO_2 into Propene and Butene
  - From ICC and Univ. Oslo
  - *Chem* **2020**, *6*, 3344-3363
- CO_2 hydrogenation to methanol and hydrocarbons over bifunctional Zn-doped ZrO_2/Zeolite catalysts
  - From Univ. Torino, KAUST, Univ. Oslo
  - Accepted, *Catal. Sci. Technol.*
- Analytical Review of Life-Cycle Environmental Impacts of Carbon Capture and Utilization Technologies
  - From Univ. Sheffield, TATA Steel
  - Accepted, *ChemSusChem*

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuel and OlefinS.
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Conclusions

- The COZMOS project aims to combine two catalytic processes into a single catalyst and process for the conversion of CO_2 into C_3 hydrocarbons
- The goal is to exploit Le Chatelier's principle to drive equilibrium-limited CO_2 conversions to higher, industrially relevant levels.
- The conversion of CO_2 to C_3 products is thermodynamically accessible in an industrially relevant temperature window.
- Important to optimize process conditions to minimize recycle and energy requirements
- Vision is a flexible process that can vary the C_3 product to fit the needs and limitations of different locations.

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuel and OlefinS.
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CONVERGE technology for efficient methanol production: Energy and Environmental analysis

Petrescu Letitia

International workshop on CO2 capture and utilization/ Eindhoven/ 16-17 February 2021

Objectives

» Green methanol for biofuel production using waste feedstock as raw-material

Biomass waste

State-of-the-Art

CONVERGE

Technologies involved

Green methanol

Biofuel

» The waste feedstock (from 4 different regions) will be characterized and used in process modeling and simulation tasks; its supply chain will represent important data for LCA

» The optimum economic layout will be identified for CONVERGE technology

» LCA will compare the environmental impacts of CONVERGE to other green methanol production processes

» Evaluation of social impact

CONVERGE concept

» Combines five innovative processes

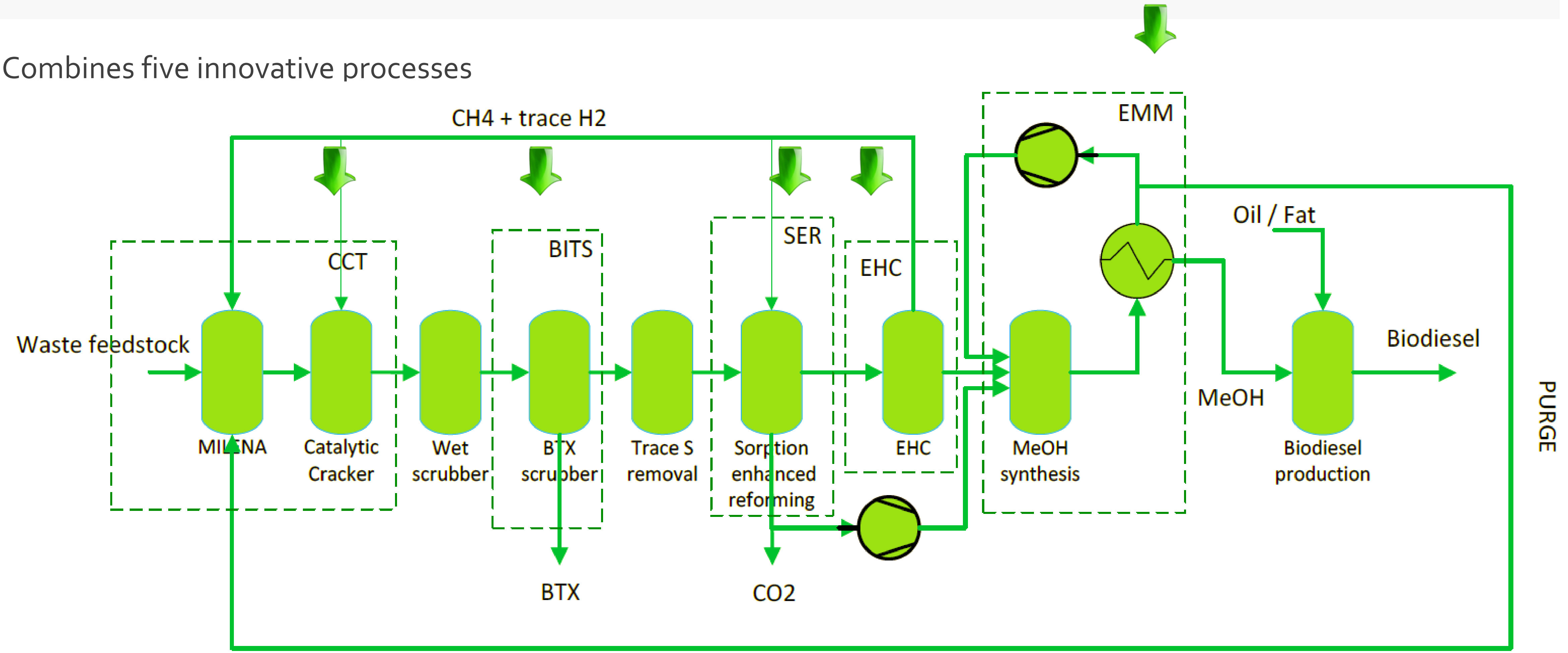


Figure 1. CONVERGE process flowsheet

CONVERGE main units

CCT	BITS	SER	EHC	EMM
» Catalytic cracking of tars from an indirectly heated gasifier to below green C8 » **Advantage:** • Removes the separation of high molecular weight tars from downstream processes, also allowing other by-product fuels, i.e. CH_4 and methanol purge to fire the gasification and SER units	» Recovery of refinery products including aromatics for green C6-C8 fraction (BTX) » **Advantage:** • Avoid the need to pressurize all the producer gas to perform hydrodesulphurization (HDS), and create an extra revenue stream that will also receive positive price pressure in a future carbon-constrained world	» Sorption-Enhanced Reforming of C1-C6 for excess-carbon removal, and H_2 production » **Advantage:** • Lowers the temperature at which reforming is performed, and produces a CO_2 stream that only partially needs to be compressed for methanol production	» Highly efficient electrochemical compression of green H_2 with by-product fuel » **Advantage:** • Elimination of mechanical compression costs for H_2 compression. In combination with SER and EMM compression costs are driven to an absolute minimum	» Enhanced Methanol Membrane to ensure efficient green biodiesel production » **Advantage:** • Due to in situ separation of inhibition products the catalyst for methanol production operates more efficiently as the composition remains further away from equilibrium

CONVERGE - Advantages

Technical

- ↘30% of energy losses related to biodiesel production → ↗12% in production;
- **Syngas treatment:** ↗5% in C/H_2 purity → ↗17% overall carbon usage;
- **SER:** reduce the H_2 production and CO_2 separation from 2 MJ/kgCO_2 down to 1.2 MJ/kgCO_2;
- **EHC:** reduce the purification and compression work from 16 MJ/kgH_2 down to 12 MJ/kgH_2;
- **Enhanced Membrane Methanol synthesis:** single pass conversion >33% → size reduction of the methanol reactor;

Economic

- 15% ↘ of CAPEX for the overall process;
- 10% ↘ of OPEX;

Environmental

- Reduction of CO_2 emissions by 0.2 kgCO_2/kgMeOH as consequence of higher production efficiency;
- Reduce the biomass transportation costs as consequence of the process flexibility and supply chain evaluations for 4 distinct geographical regions;

WP5 - Details

WP objectives

- Definition of the Base Case (BC) and CONVERGE Case

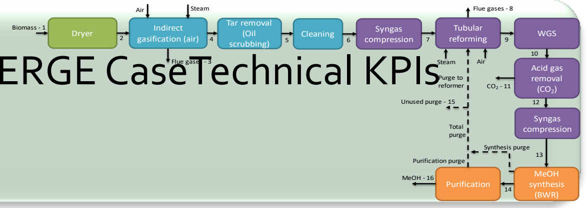
Steps to reach the objectives

- Identification of possible raw-materials for BC and CONVERGE Case
- Identification of the main blocks for BC and CONVERGE Case
- Identification of the best operating conditions of various sub-units
- Construction of BC and CONVERGE Case process flow-diagram

Tools to reach the objective

- Process flow-modelling tools (i.e. Aspen Plus)
- Validation of the models
- Discussions, side-meetings, e-mails, skype calls

Results obtained



- Detailed mass & heat balances for BC and and CONVERGE CaseTechnical KPIs (e.g. cold gas efficiency)
- Plants economics (e.g. levelized cost of fuel)

CarbON Valorisation in Energy-efficient Green fuels

WP 5 Objectives

Energy efficiency

Costs

Environmental impact

Social Impact

Comparison between state-of-the-art and CONVERGE technologies

Base case

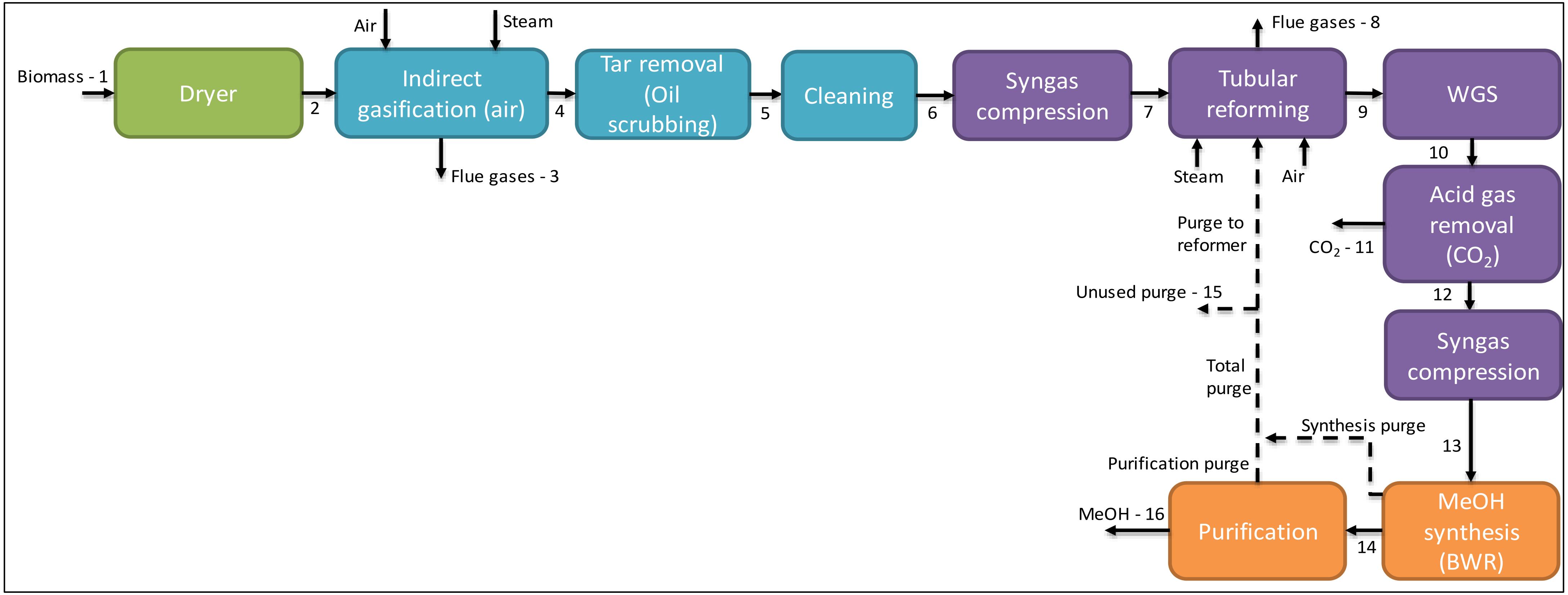


Figure 2. Simplified process flow-sheet of the Base Case

Technical analysis – Case studies

CONVERGE Case

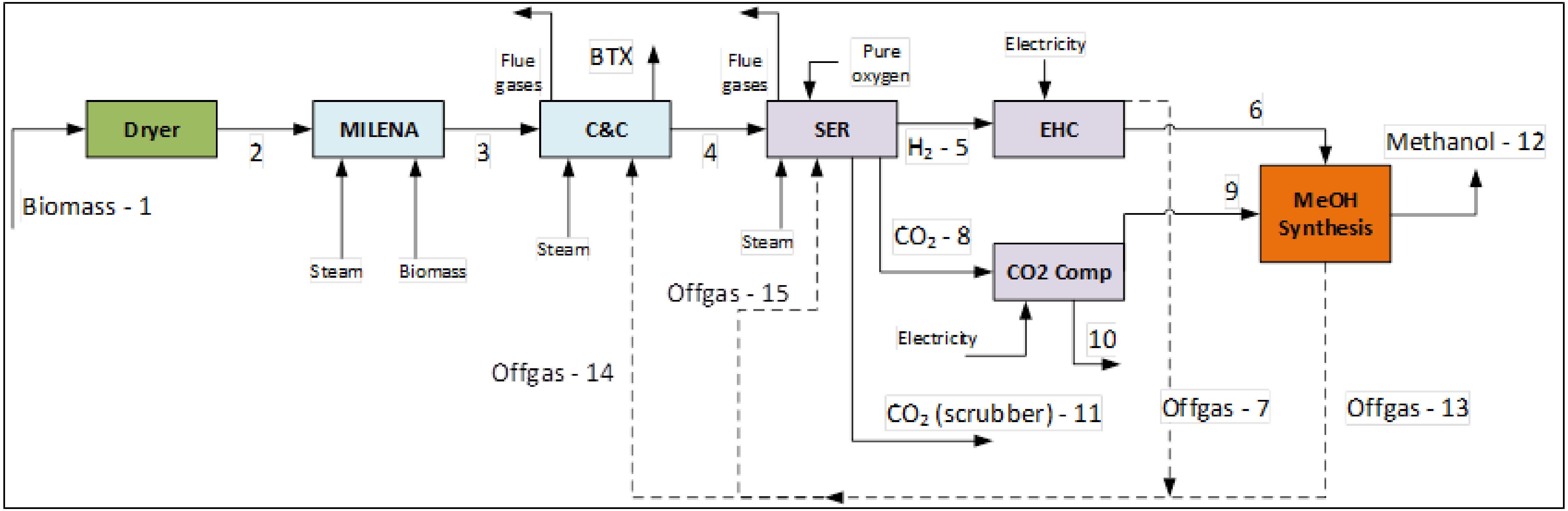


Figure 3. Simplified process flow-sheet of the CONVERGE Case

Technical analysis

Table 1. Case studies comparison

PROCESS	BASE CASE (BC)	CONVERGE CASE
Biomass drying	Tube bundle drier	Tube bundle drier
Biomass conversion (Syngas production)	Indirect gasification (MILENA) Atmospheric pressure Air and steam	Indirect gasification (MILENA) Atmospheric pressure Air and steam
Tar removal	Oil scrubbing (OLGA)	Catalytic Cracking
Syngas cleaning and conditioning	Water scrubbing Compression up to 22 bar Tubular reforming WGS bypassed Acid gas removal - MDEA Compression up to 72 bar	Water scrubbing - - - SER+CO_2 compression (up to 80 bar) ECC (compression up to 80 bar)
Methanol synthesis	Boiling water reactor	Membrane reactor
Methanol purification	Stripping of light gasses and water separation	Stripping of light gasses and water separation

Technical analysis

Table 2. Examples of possible biomass

	Forest residues	Cereal straw	Residual lignin
C	50.71	48.12	57.80
H	6.08	6.57	6.20
O	42.84	48.18	33.83
N	0.38	0.45	0.80
S	0.06	0.07	0.13
Cl	0.09	0.30	0.00
Fixed C	17.93	21.02	27.80
Volatile matter	82.07	78.98	72.20
Ash	1.00	6.70	0.10
Moisture	35.00	7.80	52.00
LHV [MJ/kg]	11.55	15.37	11.01

Table 3. Global plant performance

CGE section		Base Case	CONVERGE	CONVERGE Optimized
Global (methanol)		58.59%	42.55%	49.43%
Global (methanol +BTX)		-	51.45%	58.75%
MILENA	Gasifier	82.73%	84.41%	84.43%
Cleaning		99.79%	97.89%	94.96%
Reformer	SER	104.79%	88.34%	94.27%
WGS+CO_2 separation		99.98%	-	-
Methanol synthesis		68.36%	82.64%	81.72%
Methanol purification		97.84%		

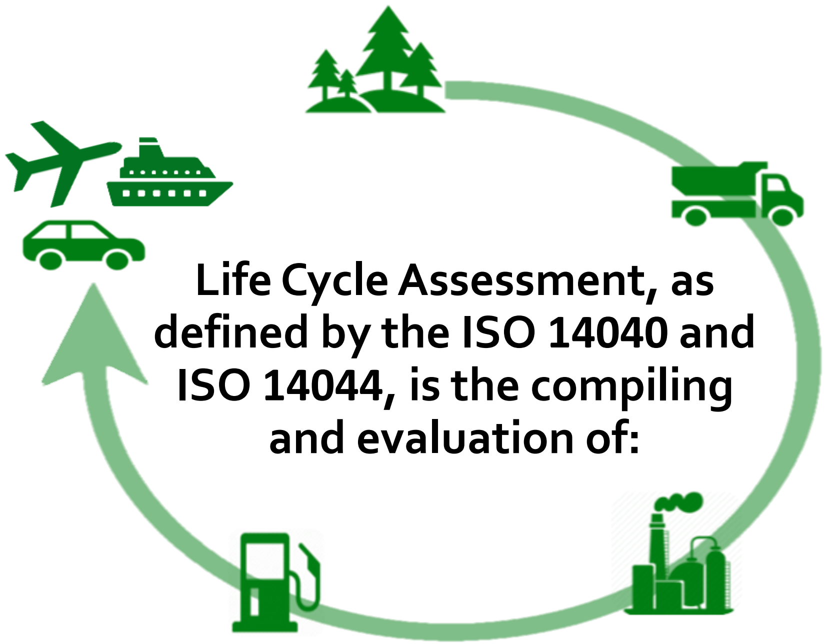
Technical and economic analysis for BC

Table 4. Case studies comparison

Technical KPI		BASE CASE (BC)		
Plant capacity		10 MW_{LHV}	100 MW_{LHV}	300 MW_{LHV}
MeOH production	ton/d	25.1	251	753
CO_2 separated	ton/d	27.7	277	831
CGE global	%		58.6	
Costs		**BASE CASE (BC)**		
Total Capital Investment	M€	39.1	206	424
	M€/y	7.09	43.8	101.6
Total yearly cost	€/ton	1010	525	406
LCOF	€/MWh	183	95	73

CONVERGE
CarbON Valorisation in Energy-efficient Green fuels

Environmental analysis



Life Cycle Assessment, as defined by the ISO 14040 and ISO 14044, is the compiling and evaluation of:

- the inputs
- the outputs and
- potential environmental impacts of a product/system during its lifetime.

» Life Cycle Assessment Steps

- Goal and scope definition
- Life cycle inventory
- Life cycle impact assessment
- Interpretation

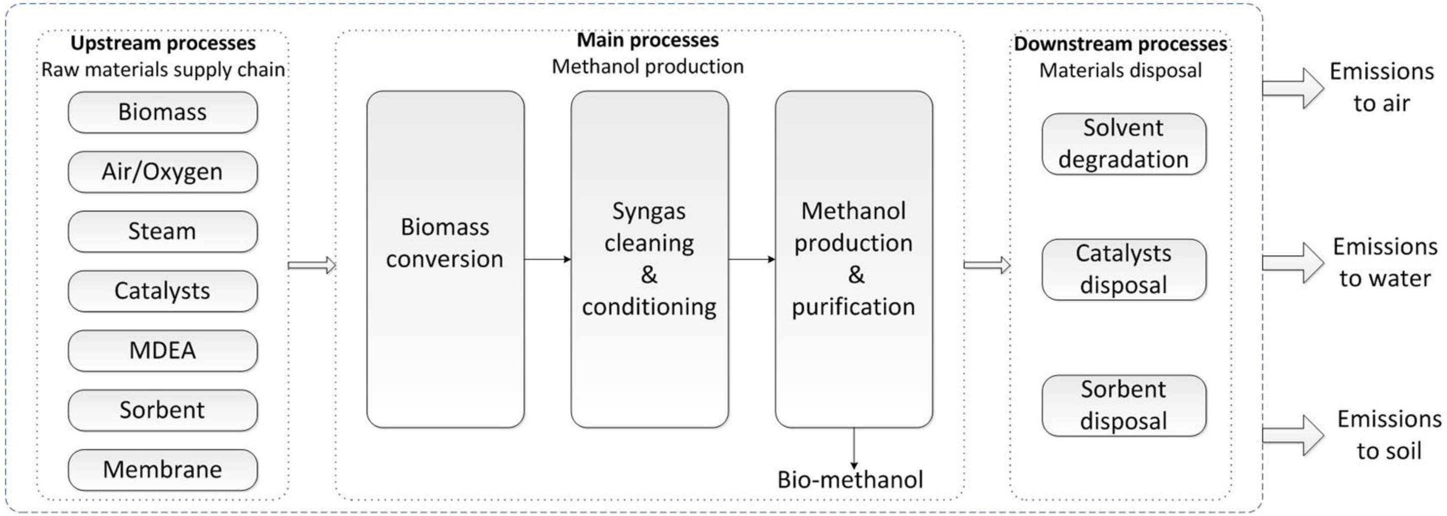
Environmental analysis

Goal and scope definition

» **Goal:** Evaluate and compare the environmental burden of bio-methanol production proposed in the CONVERGE technology with other technologies for bio-methanol production.

» **Scope:**

- boundary conditions



- functional unit - one tone of MeOH
- plant lifetime - 20 years
- plant location - Europe: Sweden

Life cycle inventory

» Quantification of inputs and outputs for a product/process throughout its life cycle

- Energy
- Raw materials
- Air emissions
- Water emissions
- Soil emissions

Life cycle impact assessment

thinkstep GaBi Product Sustainability Performance

ReCiPe Impact Assessment Method

- Global Warming Potential (**GWP**)
- Freshwater Eutrophication Potential (**FEP**)
- Ozone Depletion Potential (**ODP**)
- Fossil fuel Depletion Potential (**FDP**)
- Freshwater Ecotoxicity Potential (**FETP**)
- Human Toxicity Potential (**HTP**)
- Mineral Depletion Potential (**MDP**)
- Photochemical Oxidant Formation Potential (**POFP**)
- Terrestrial Ecotoxicity Potential (**TETP**)

Environmental analysis

Interpretation

Table 5. LCA Results

KPI	Units	Base Case	CONVERGE
GWP	kg CO_2 eq./ tMeOH	1305.4	1470.47
ODP*10⁹	kg CFC-11 eq./ tMeOH	5.85	4.89
FDP	kg oil eq./ tMeOH	6.15	8.35
FETP	kg 1,4-DB eq./ tMeOH	0.51	0.19
HTP	kg 1,4-DB eq./ tMeOH	36.69	7.06
MDP	kg Fe eq./ tMeOH	2.51	2.81
POFP	kg NMVOC/ tMeOH	0.15	0.149
TETP *10³	kg 1,4-DB eq./ tMeOH	9.18	4.61

Concluding remarks

» Different types of biomass are/will be considered in the CONVERGE project for biomass transformation into bio-methanol

» The attention was focused on forest residues biomass

» Cereal straw and residual lignin will be considered in future evaluations

» Calculation of technical KPIs for CONVERGE concept have been performed

» Economic analysis is an on-going task

» Environmental impact was evaluated for the main process (base case and CONVERGE concept) but upstream and downstream processes should be included in the analysis (on-going task)

Thank you for your attention!

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Acknowledgements

The CONVERGE project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 818135

CONVERGE

CarbON Valorisation in Energy-efficient Green fuels

INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILIZATION

TU/E - EINDHOVEN - 16-17 FEBRUARY 2021

Opening & Plenary Sessions (chairperson Fernanda Neira D'Angelo)

9:30-10:00	All coordinators - Introduction to projects
10:00-11:00	Dr. K. Bakke - Northern Lights – concept, plans and future

ORGANIZED BY

SPONSORED BY

Northern Lights

A European CO_2 transport and storage network

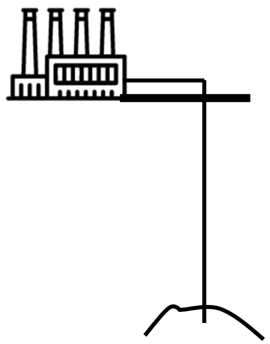
https://northernlightsccs.eu/

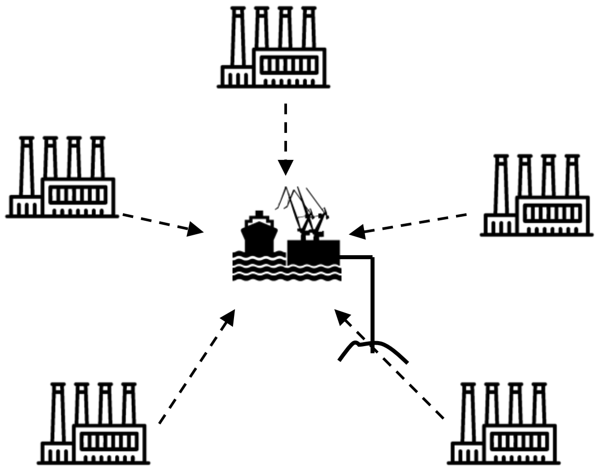
equinor

TOTAL

Agenda

- Introduction
- Separating source and sink
- Longship
- What is Northern Lights?
- Storage experience
- Is there a business opportunity?
- Some challenges
- Summary
- Q&A





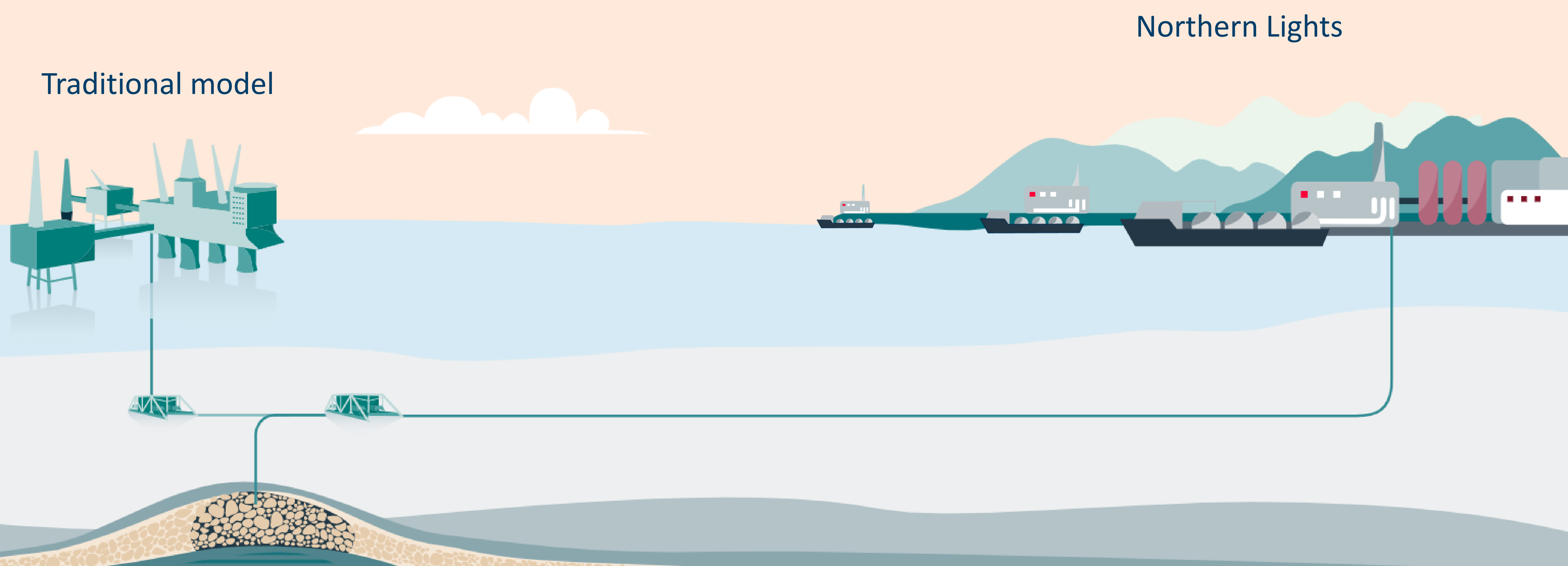
Separating source and sink

01.03.2021

SEPARATING SOURCE AND SINK

Traditional model

SEPARATING SOURCE AND SINK

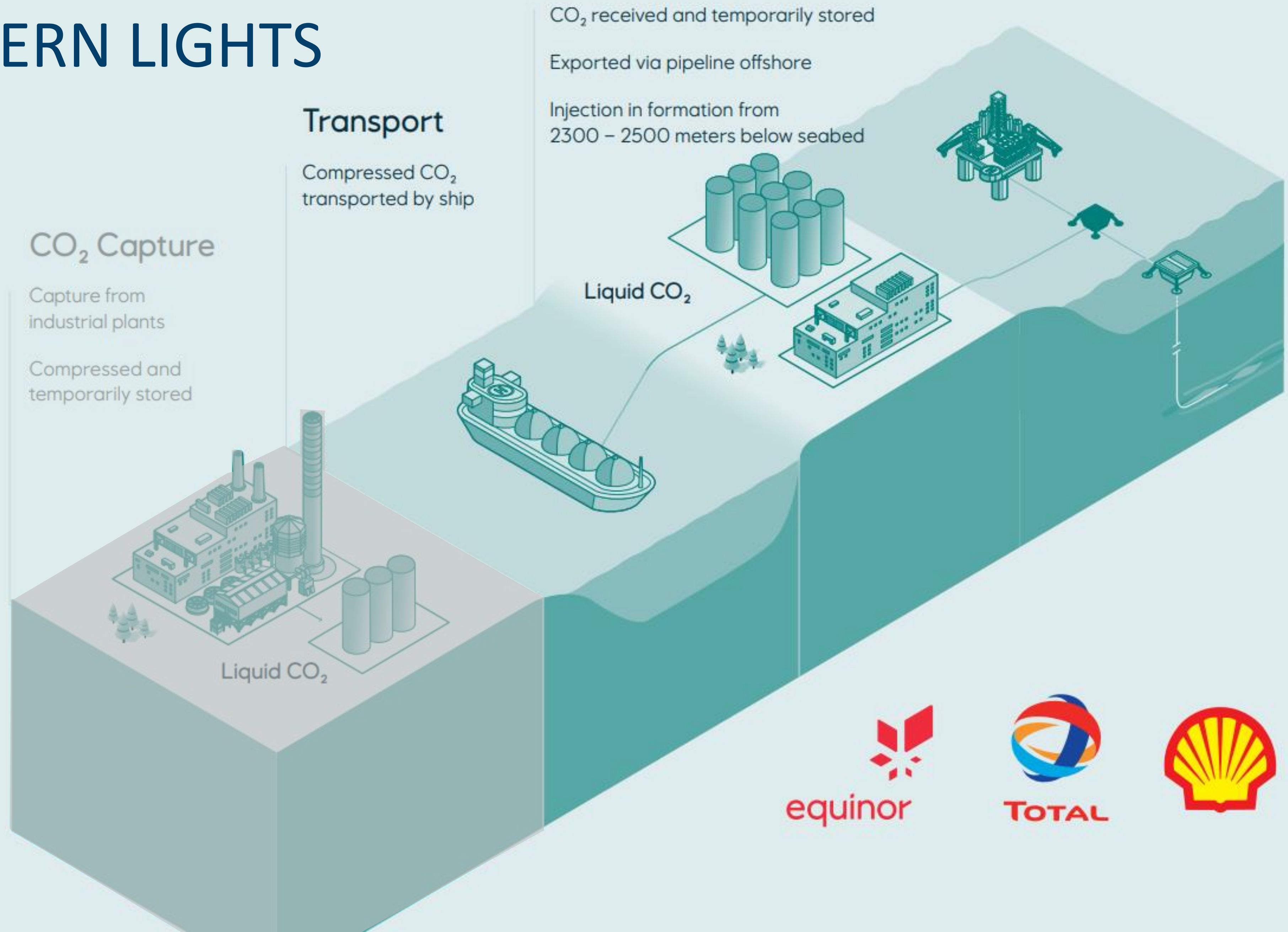


Longship

01.03.2021

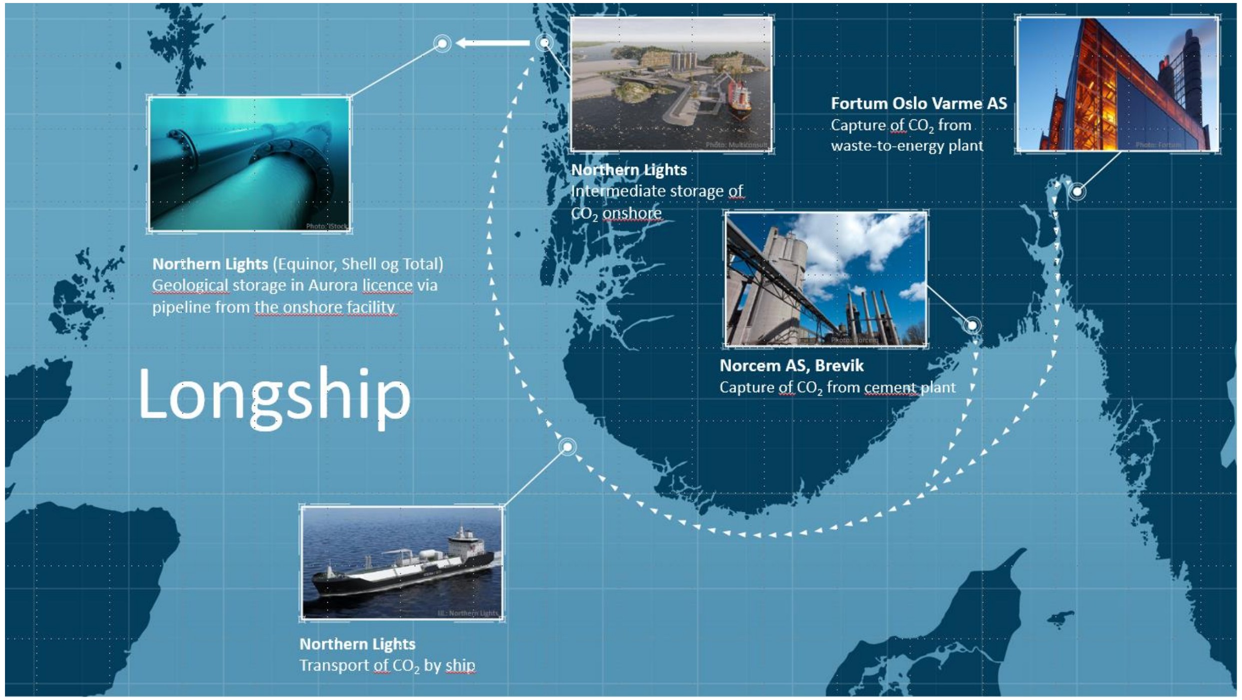
NORTHERN LIGHTS

Injection and storage



Longship in summary

- Norcem facilities with start-up in 2024
- Partial funding of Fortum Oslo varme (FOV)
  - A FID must be made by FOV within three months of EU Innovation fund announcing awards in the second round, but no later than 31. December 2024
- Northern Lights
  - Facility scope with 1,5 mtpa capacity
  - 2 ships

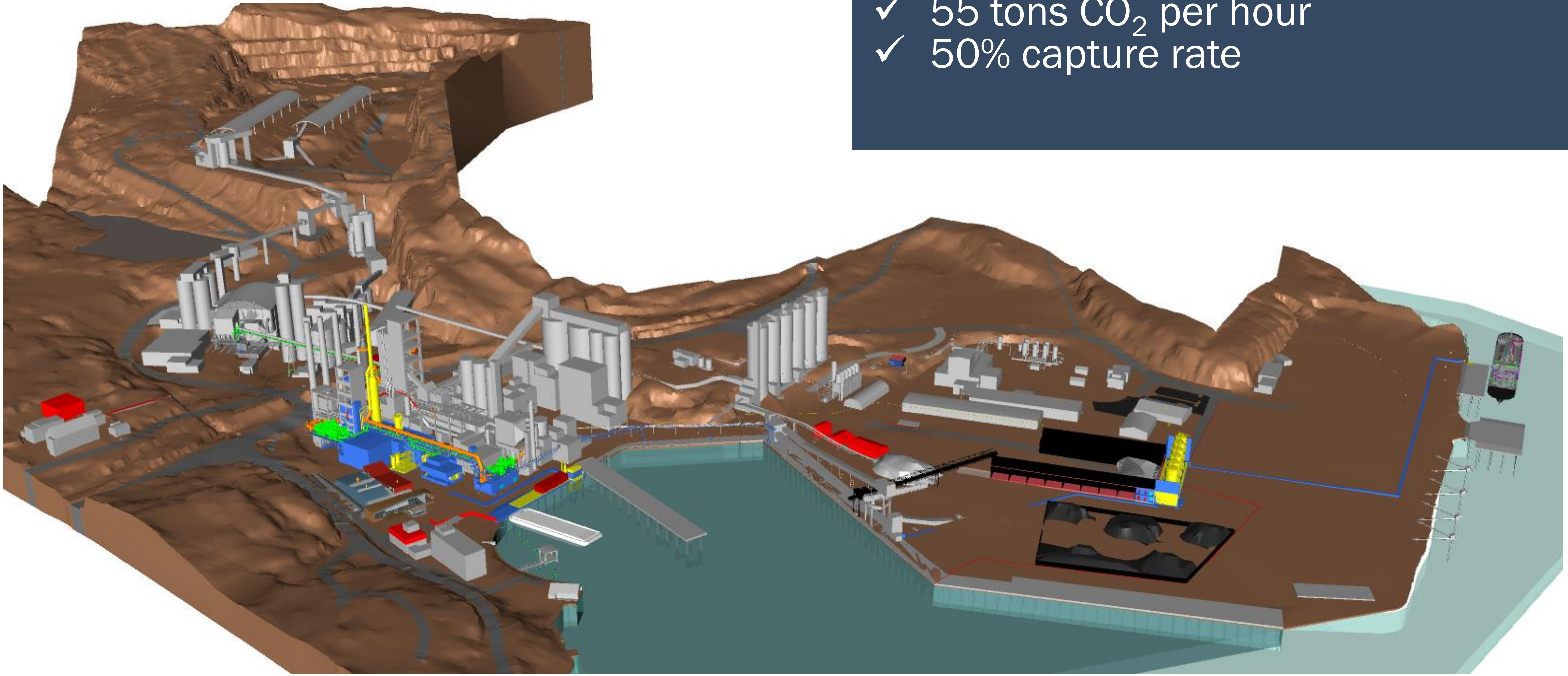


CO_2 capture Brevik

Demonstration plant

400.000 tons per year

- ✓ 55 tons CO_2 per hour
- ✓ 50% capture rate



What is Northern Lights?

01.03.2021

CO_2 TRANSPORT BY SHIP

Cargo Systems for CO_2

'LPG standard' design

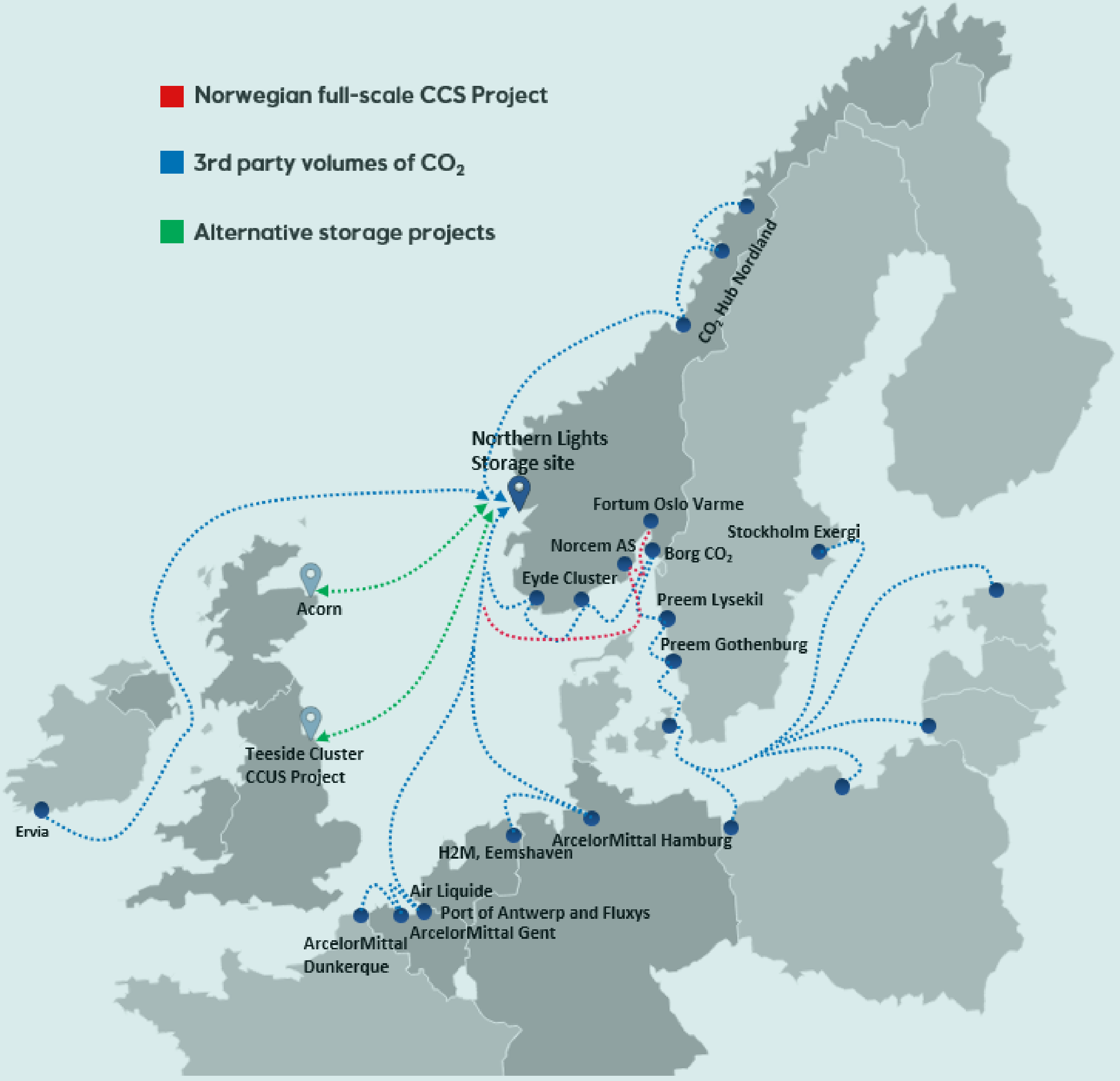
Proven concept based on food industry model

Initially two ships

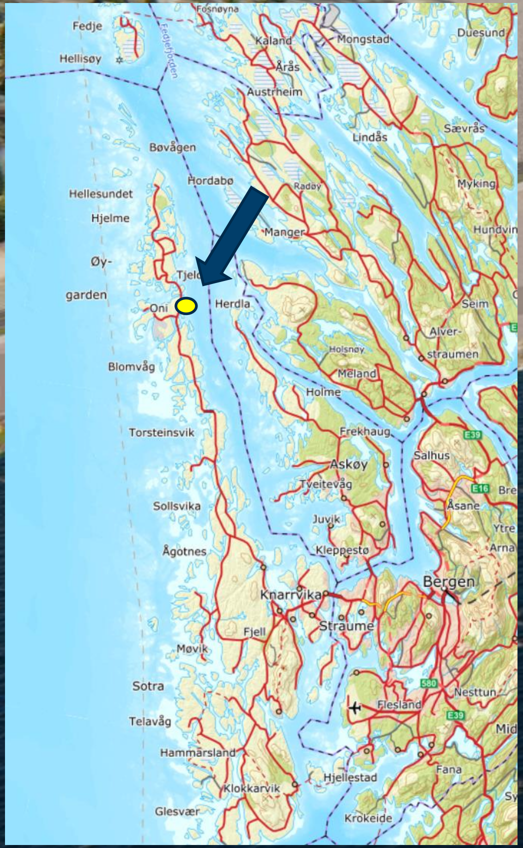
Transport capacity scalable with number of ships

A fleet is required for the planned scale-up – perfect for driving ship technology and fuels development

Delivery contract starts in Q2 2021



Northern Lights landanlegg i Øygarden



Onshore plant

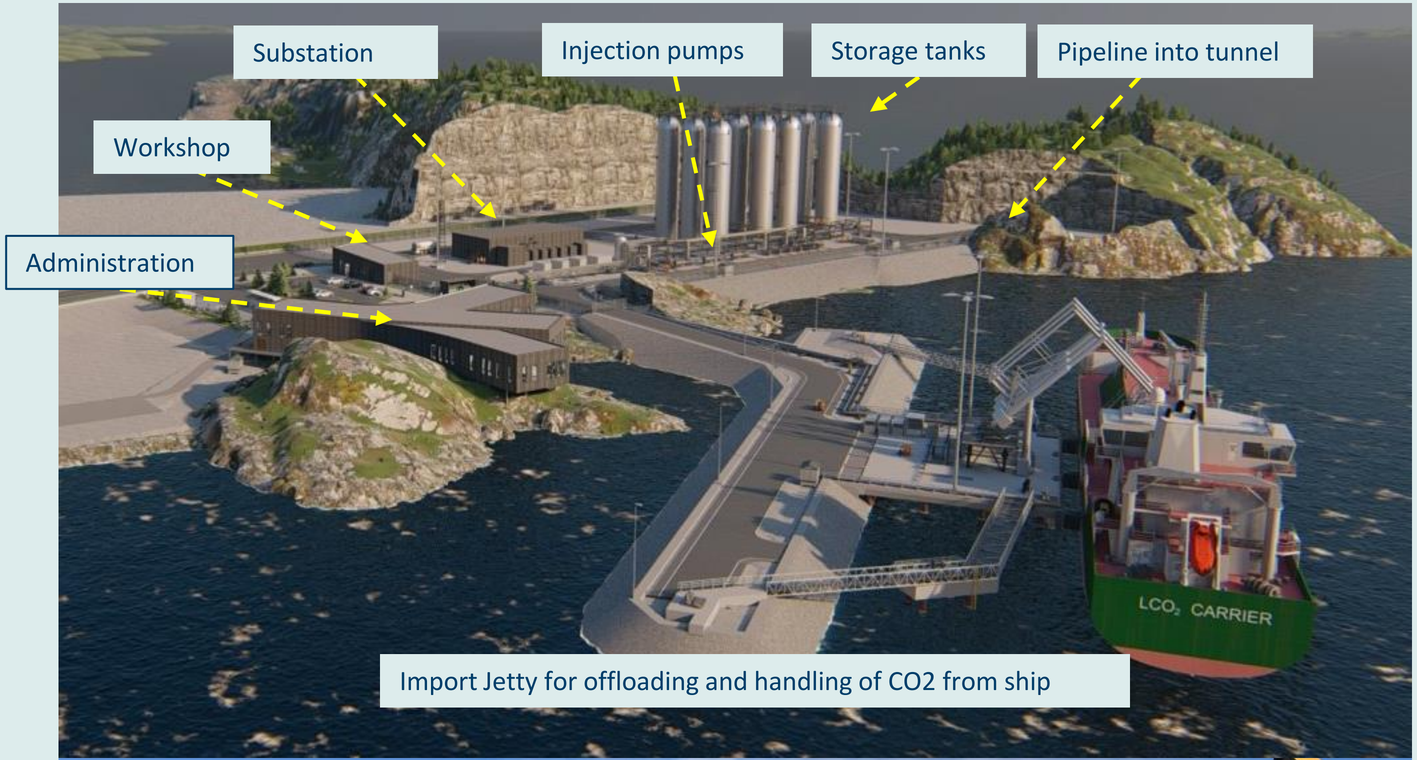
Civil works started

Preparations for jetty construction

Project office under construction

Detail engineering of plant started

Fabrication of plant starts spring 2022



Multiconsult SKANSKA KVÆRNER

Pipeline and subsea facilities

Template installed in 2019, well drilled in 2020

Fabrication of umbilical started

Fabrication of power and fibre optic control cable started

Engineering of topsides modifications at Oseberg started

Engineering of pipelay started

PetrolValves

AkerSolutions

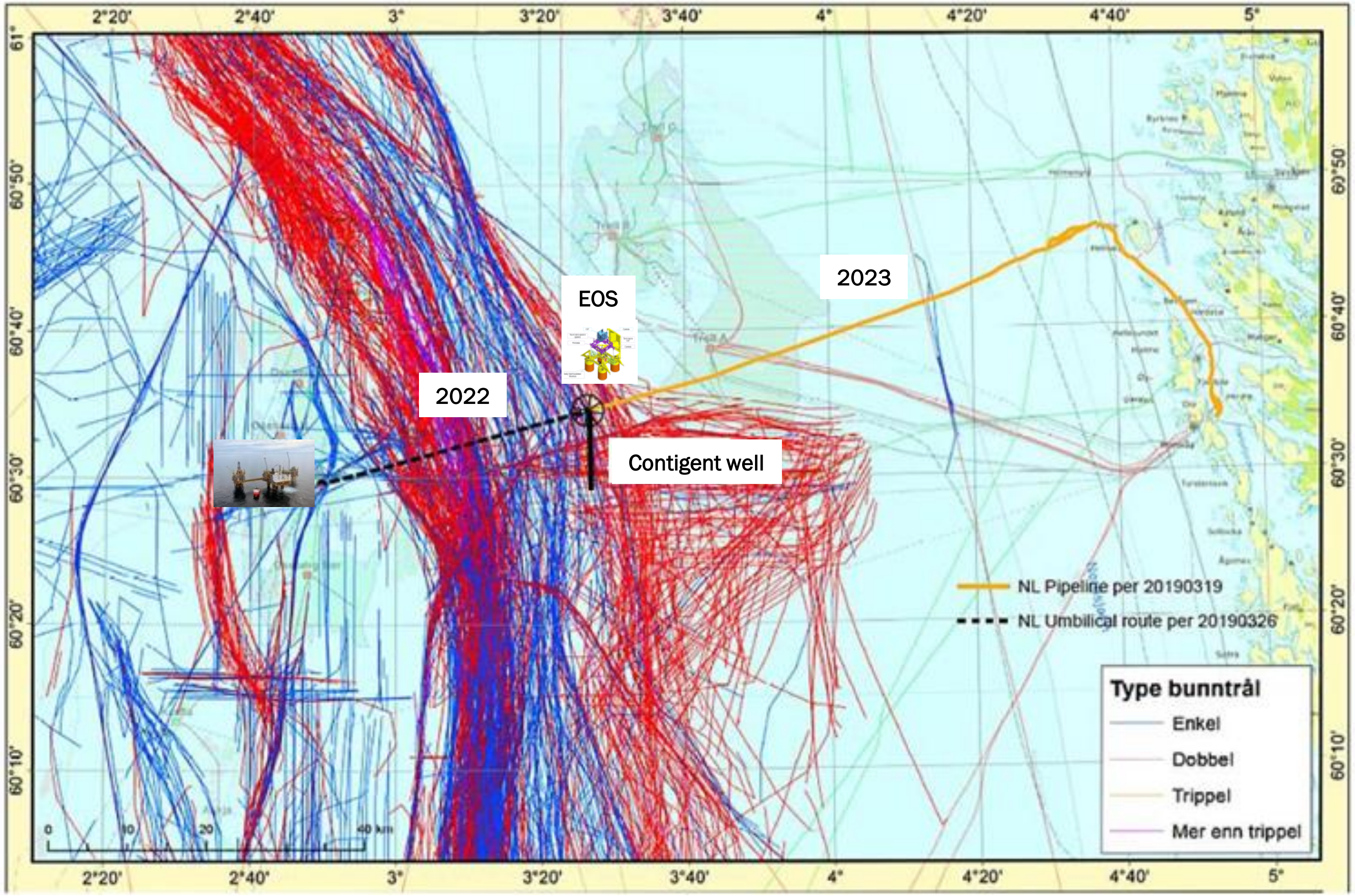
Alcatel Submarine Networks

aibel

TechnipFMC

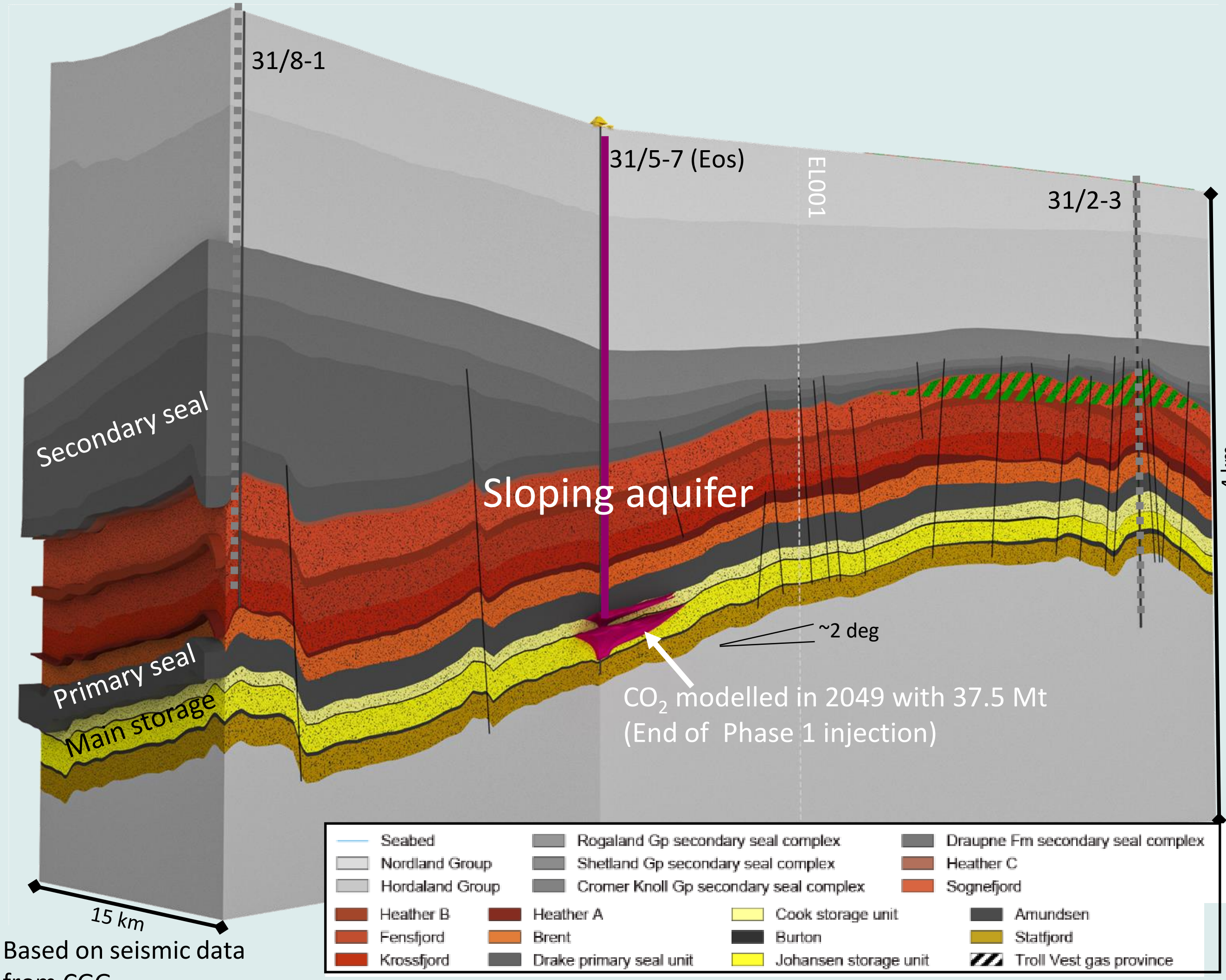
subsea 7

Northern Lighs infrastructure versus fisheries

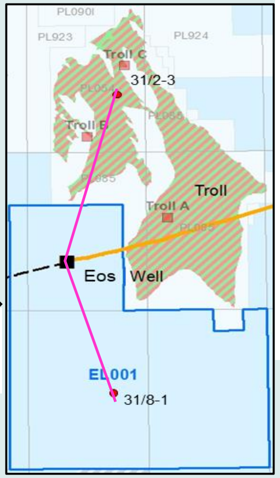


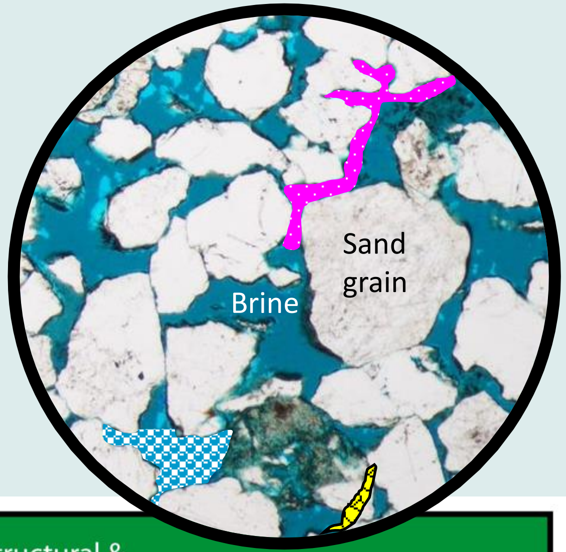
Bottom trawling activity (2018), as illustrated in IA (Phase 1) – based on satelite tracking datas of vessels

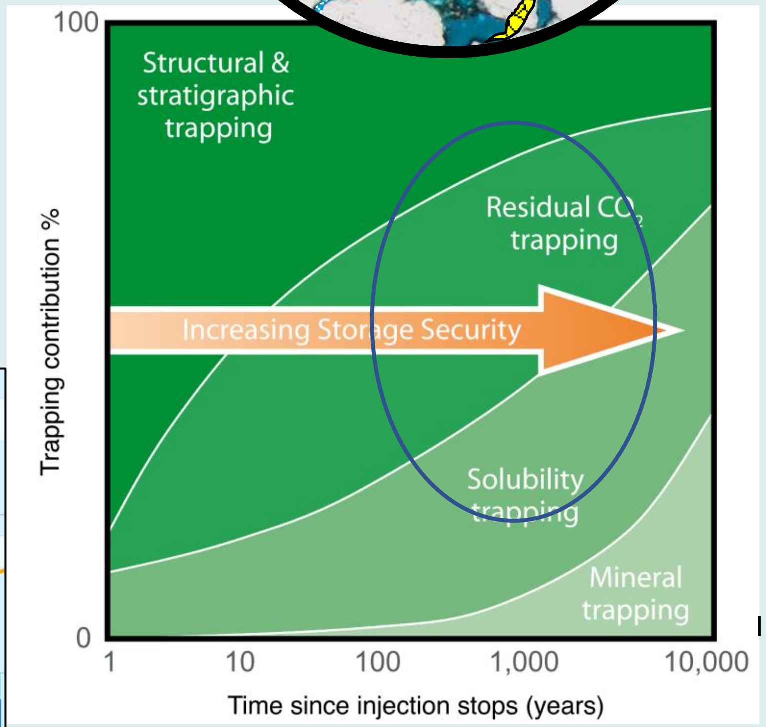
Northern Lights storage concept



Based on seismic data from CGG







IPCC, 2005

Containment and large pore volume required

Storage experience

01.03.2021

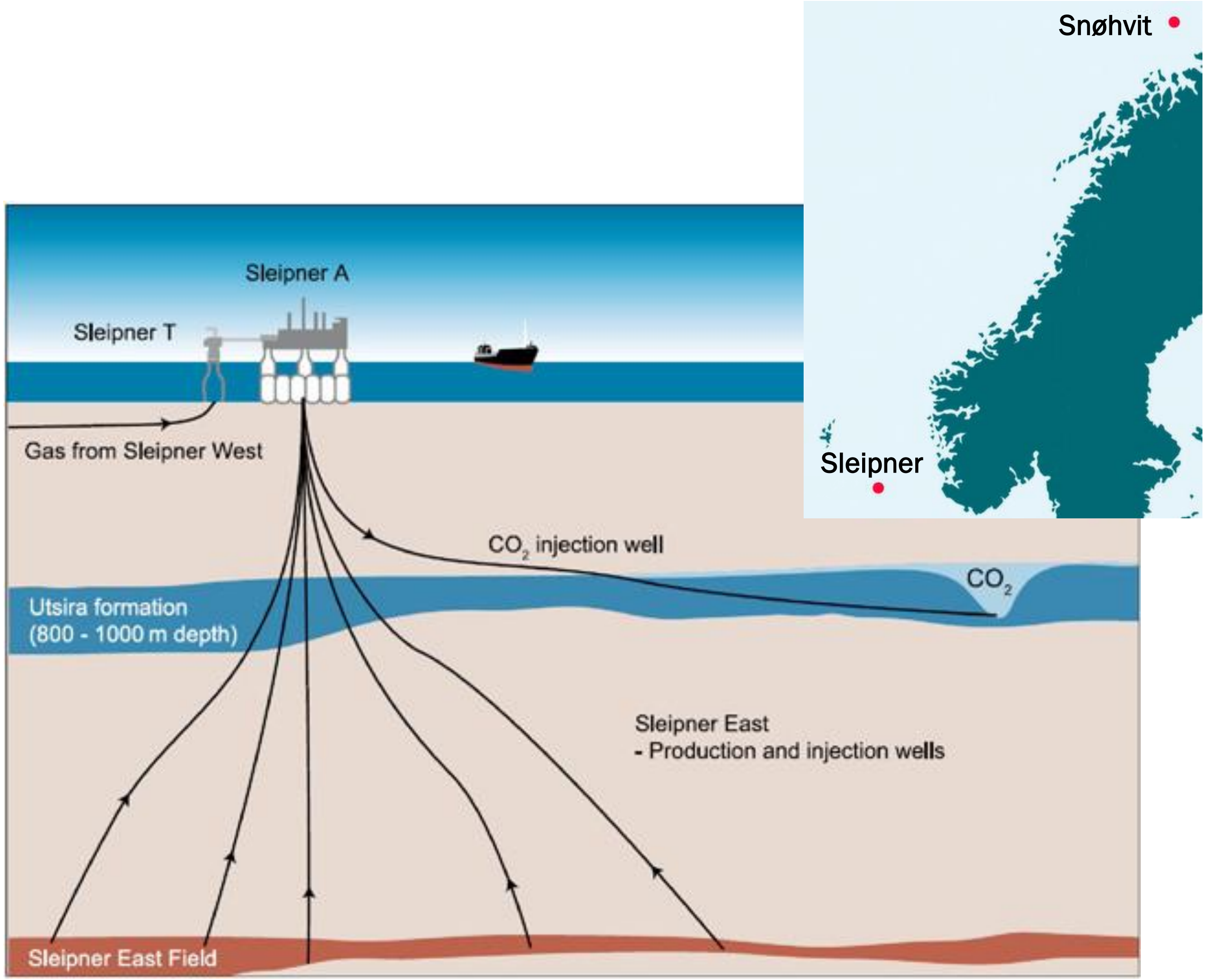
Industrial experience – Norway

Sleipner:

- Injection since 1996
- More than 18 mill t CO_2 stored*
- Frequent monitoring, many academic projects
- Data set publicly available

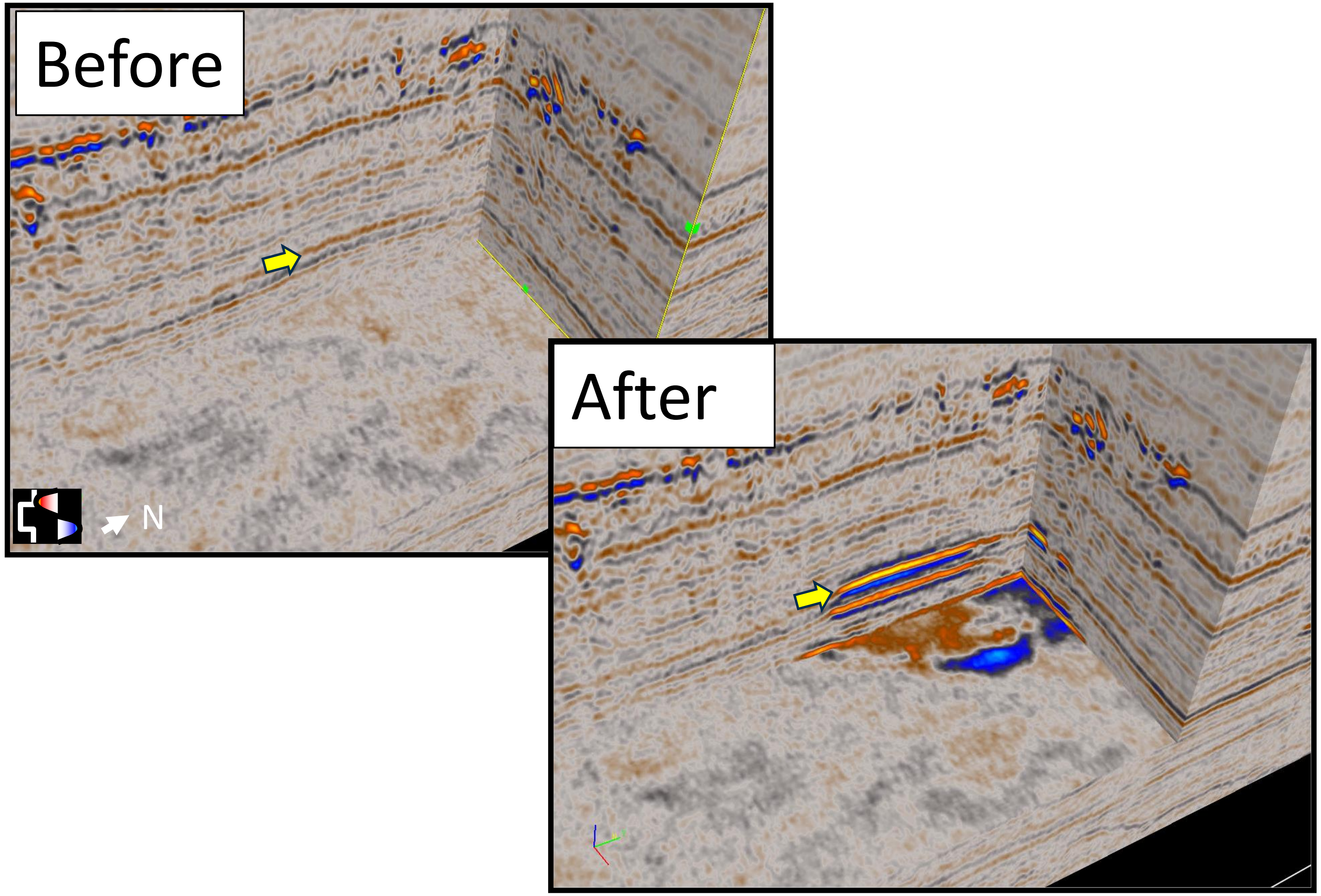
Snøhvit:

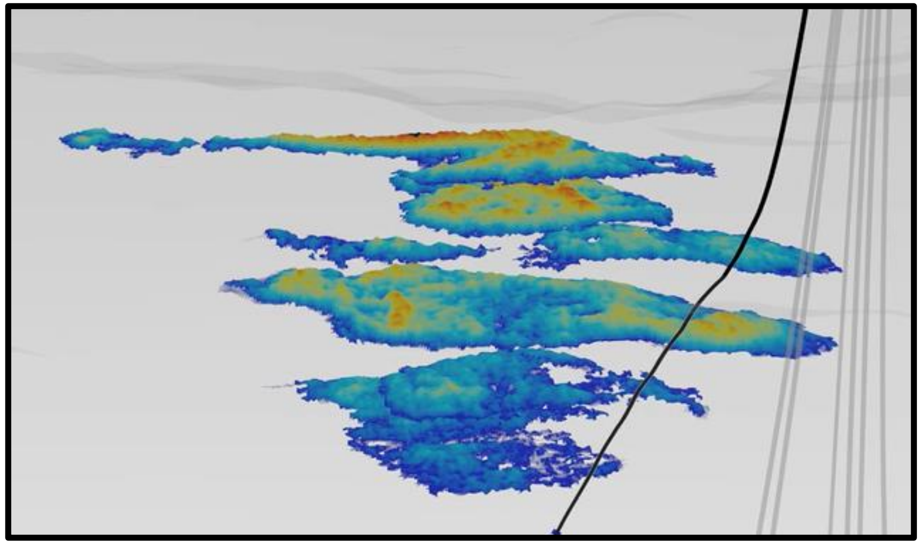
- Injection since 2008
- More than 6 mill t CO_2 stored*
- Subsea facilities



*: status end of 2019

Seismic monitoring (Sleipner)

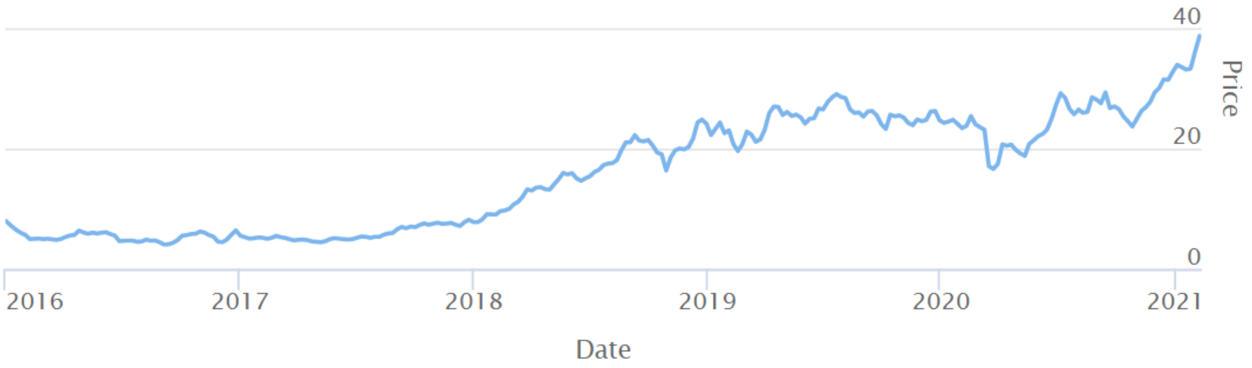




Is there a business opportunity?

01.03.2021

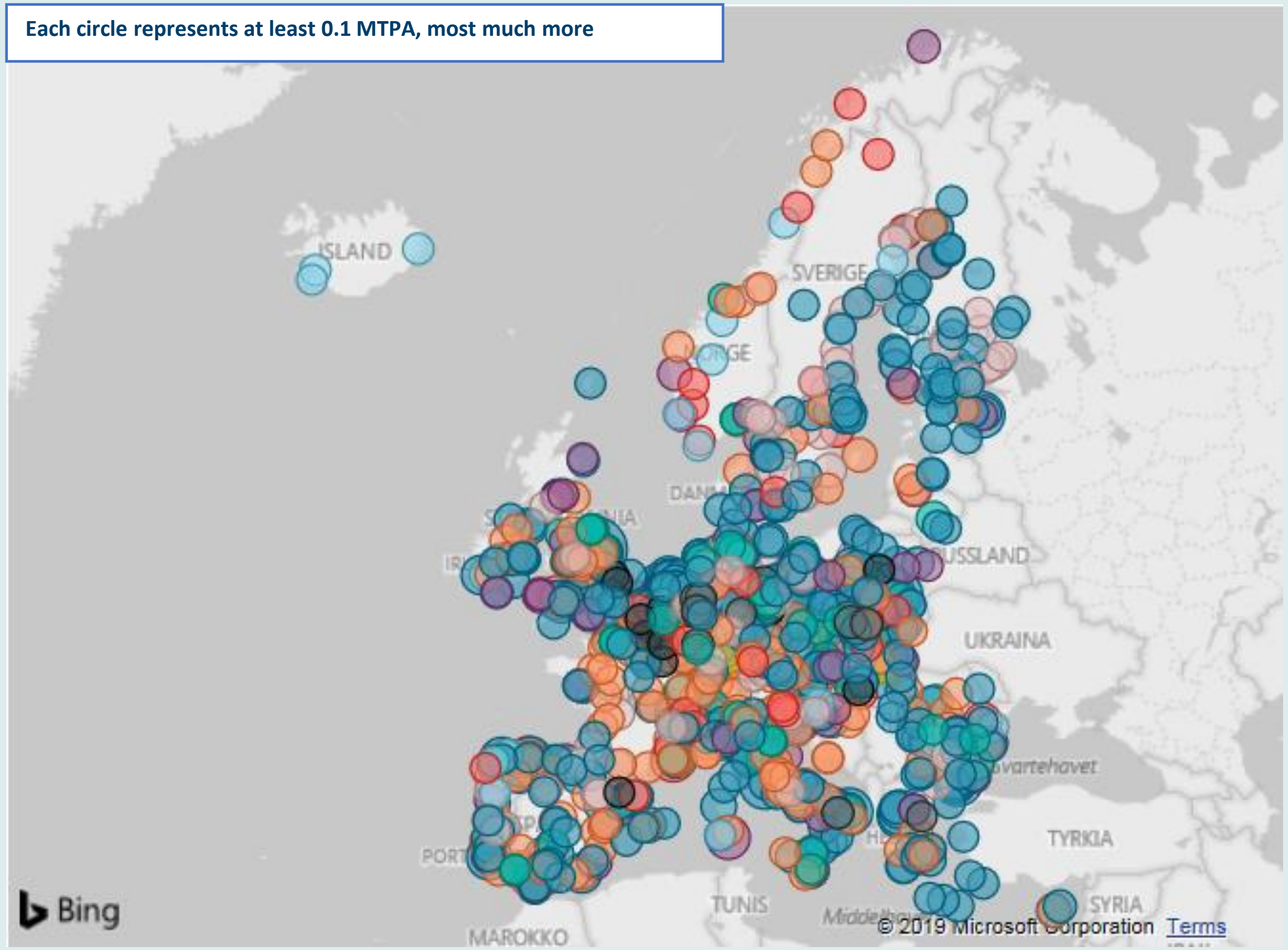
https://davidappell.blogspot.com/2019/04/eek-carbon-tax.html



https://ember-climate.org/data/carbon-price-viewer/

IS THERE A BUSINESS OPPORTUNITY?

Each circle represents at least 0.1 MTPA, most much more



endrava CARBON LIMITS

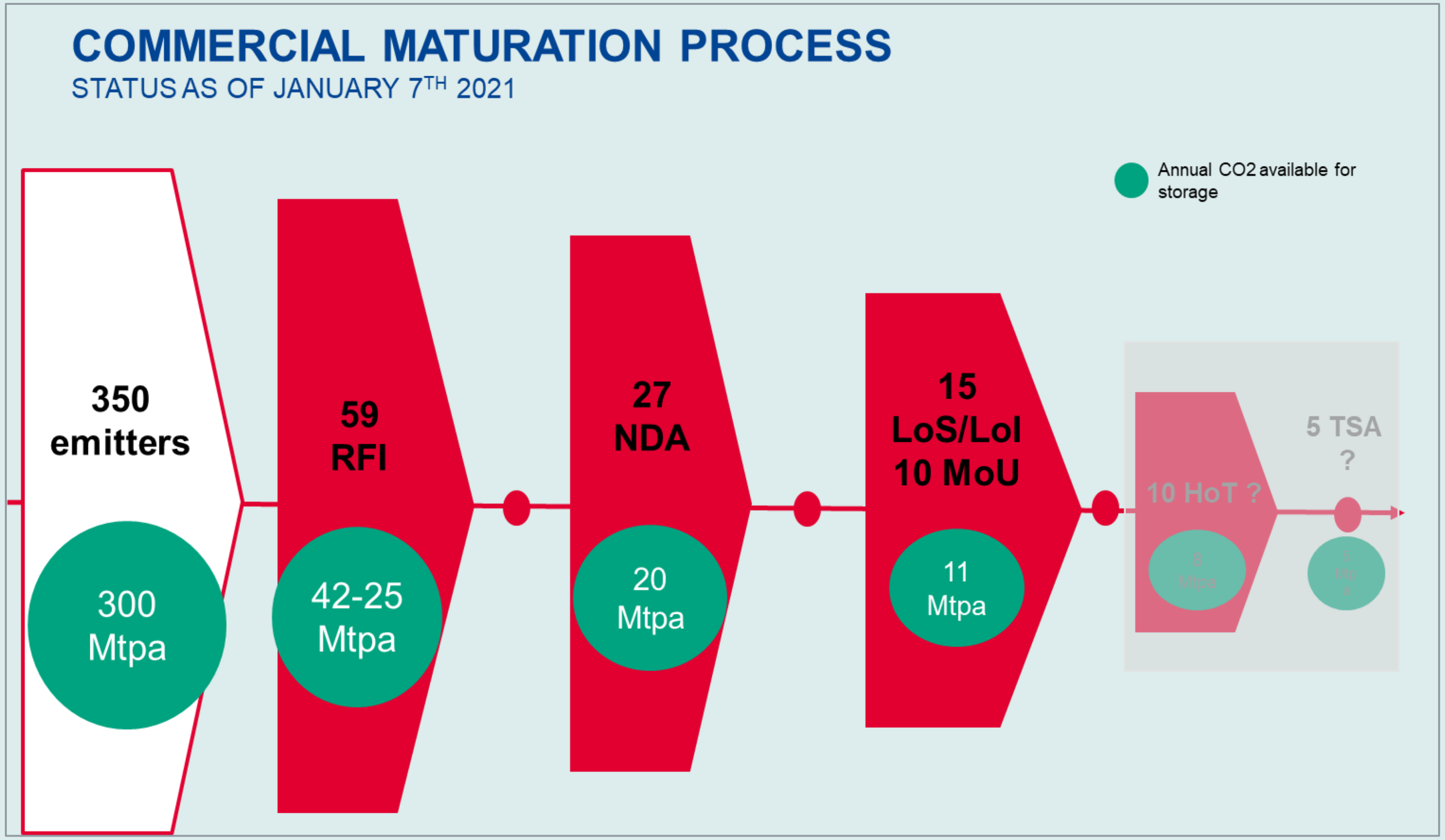
Sectors with the largest potential:

- Waste incineration and waste to energy
- Cement
- Biomass and biofuel
- Refineries
- Steel
- Natural gas
  - Hydrogen
  - Electricity
- Fertilizers
- Data centers
- Direct Air Capture

Business development funnel

MoU

- Heidelberg Group (cement), **Germany**
- Fortum Group (WtE); **Finland**
- Ervia (natural gas supply), **Ireland**
- Air Liquide (chemicals, hydrogen), **Belgium**
- Stockholm Exergi (WtE), **Sweden**
- ArcelorMittal (steel and iron), **Luxemburg**
- Preem (refineries and fuels, hydrogen), **Sweden**
- ETH Zürich, **Switzerland**
- Microsoft, **USA**



Some challenges

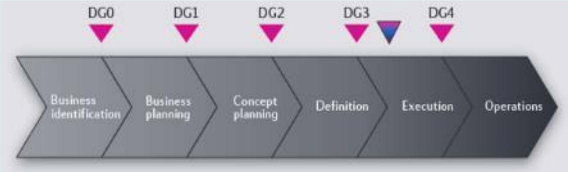
Northern Lights seen from conventional oil & gas project perspective

Normal oil & gas

Regulatory framework exists

Business case

Resource is known, permanent, validated



Markets existing and predictable

Develop project to harvest business case

- Technical maturation with DGs
- Risks identified
- Concept freeze early
- Not schedule driven

Northern Lights

Regulatory framework not in place

No business case

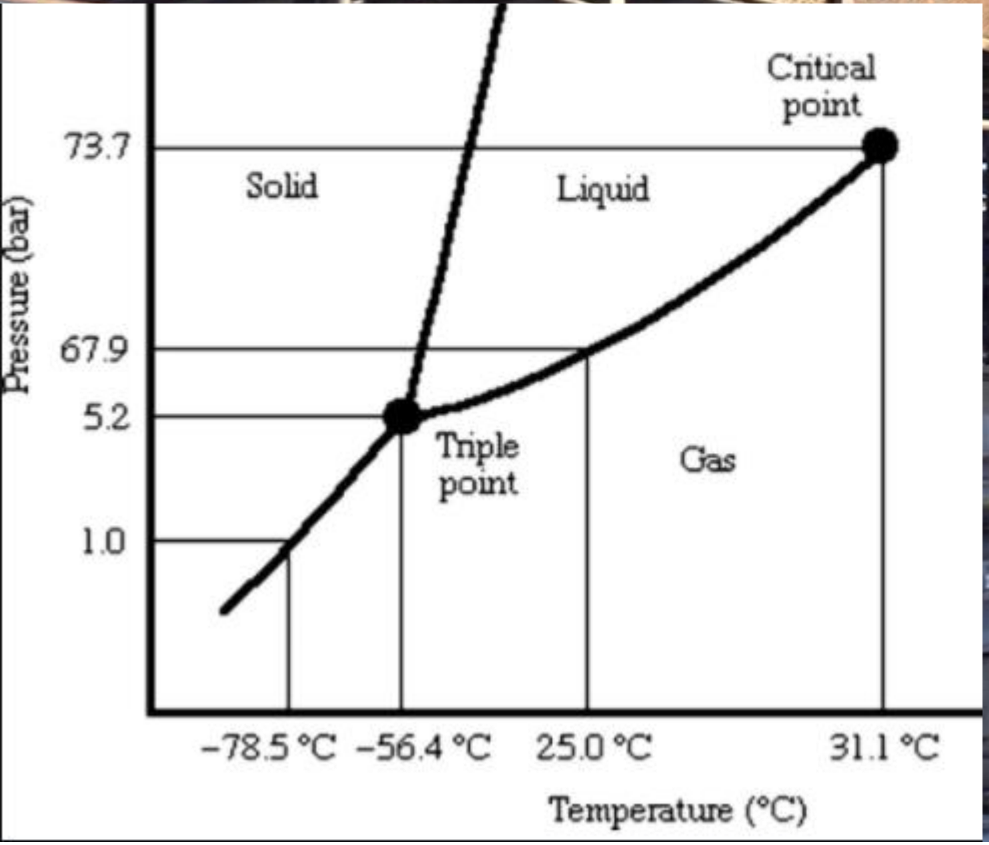
Resource is NOT known, validated:

- Not reservoir
- Not CO2

No normal markets

Develop project *to build future markets*

- Technical maturation with DGs
- Identified risks, ***and many***
- Concept ***partly*** frozen early ***(not SSV)***
- ***Schedule driven***



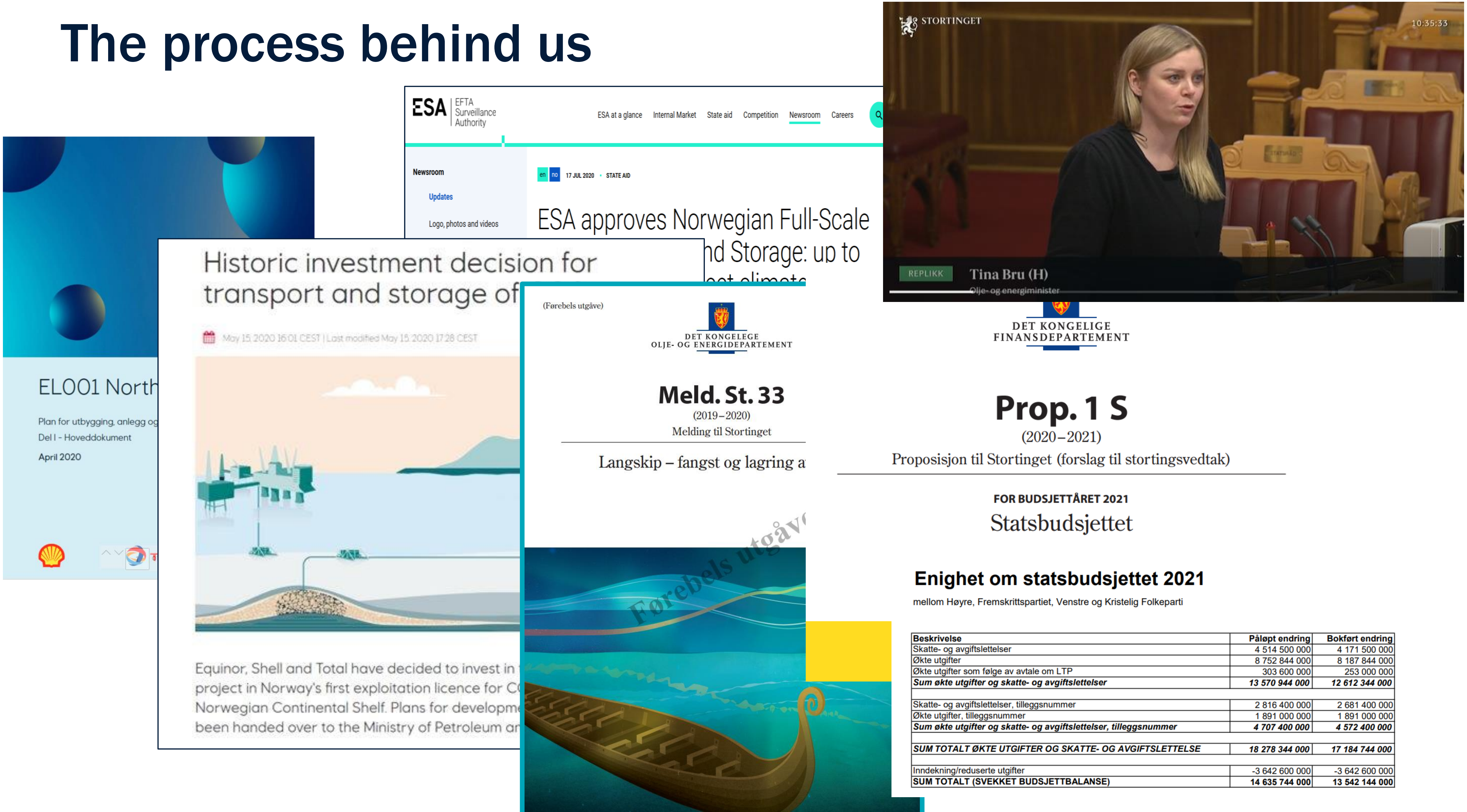
CO2 is different

- Dry ice
- Displaces air
- Noise
- Cold

Summary

01.03.2021

The process behind us



Beskrivelse	Påløpt endring	Bokført endring
Skatte- og avgiftslettelser	4 514 500 000	4 171 500 000
Økte utgifter	8 752 844 000	8 187 844 000
Økte utgifter som følge av avtale om LTP	303 600 000	253 000 000
Sum økte utgifter og skatte- og avgiftslettelser	*13 570 944 000*	*12 612 344 000*
Skatte- og avgiftslettelser, tilleggsnummer	2 816 400 000	2 681 400 000
Økte utgifter, tilleggsnummer	1 891 000 000	1 891 000 000
Sum økte utgifter og skatte- og avgiftslettelser, tilleggsnummer	*4 707 400 000*	*4 572 400 000*
SUM TOTALT ØKTE UTGIFTER OG SKATTE- OG AVGIFTSLETTELSE	*18 278 344 000*	*17 184 744 000*
Inndekning/reduserte utgifter	-3 642 600 000	-3 642 600 000
SUM TOTALT (SVEKKET BUDSJETTBALANSE)	14 635 744 000	13 542 144 000

STATUS

Project

- Majority of execution contracts awarded
- Execution started
- Site office in Øygarden in operation
- Start up mid-2024 aligned with Norcem’s plans

New company - «Northern Lights JV DA»

- Formally established on 5th Feb 21
- Regulatory obstacles passed (competitive clarifications in EU)

Q&A

Institute for Energy Technology

Research for a better future

Renewable energy

Nuclear technology

Materials technology

Digitalization

Radiopharmacy and health

Oil and gas

Industry and environment

Safety and security

CONVERGE: CarbON Valorisation in Energy-efficient Green fuels

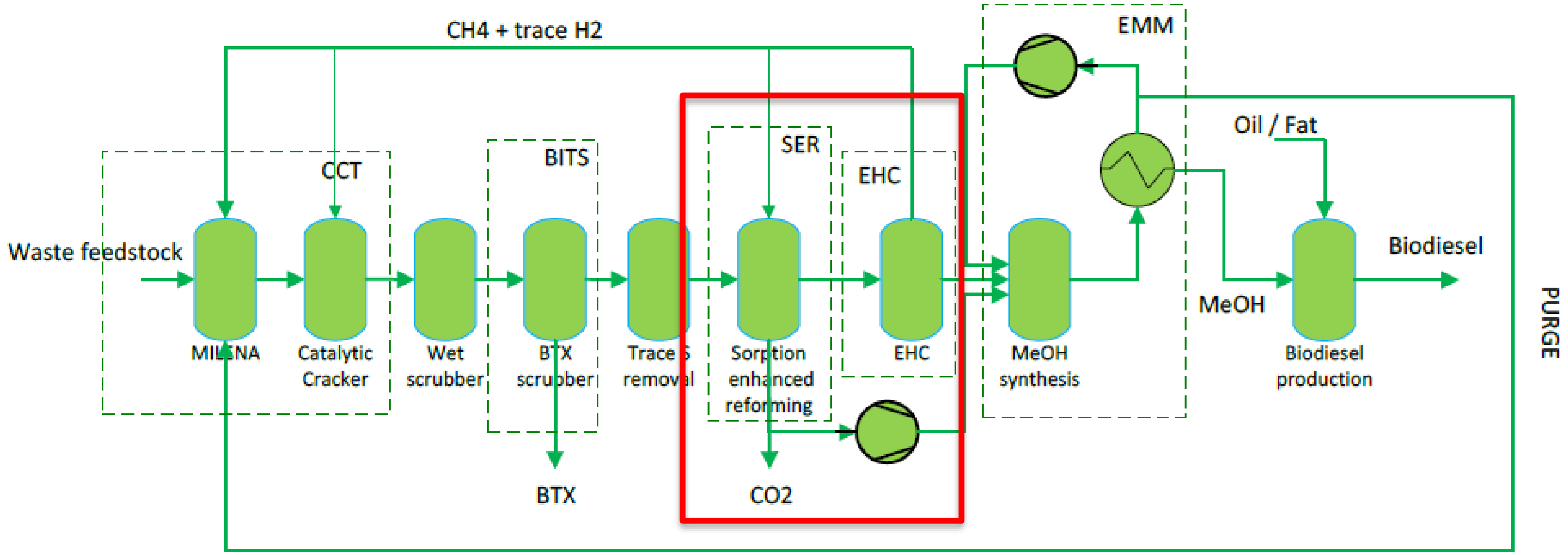
SER and SEWGS for CO2 capture: preliminary experimental results

International Workshop on CO2 capture and Utilization – February 17th 2021

CONVERGE WP3: Objectives

The main objective of WP3 is to validate the integration of the SER and EHC technologies at TRL5 in relevant operating conditions adapted to the CONVERGE concept with the following specific targets:

- Reduce the energy consumption for hydrogen production, CO_2 removal and compression to 1.2 MJ/kg CO_2
    - **Optimization of the CO_2 sorbent material used in the SER process**
    - **Development of new improved catalytic materials suited for the CONVERGE syngas**
- Extract and compress H_2 at >99.5% purity, 50 bar and at a primary energy consumption of 12 MJ/kg H_2
- Operate the SER and EHC for 500 hours on C1-C6 containing emulated syngas feed at 10 Nm^3/hr H_2 production

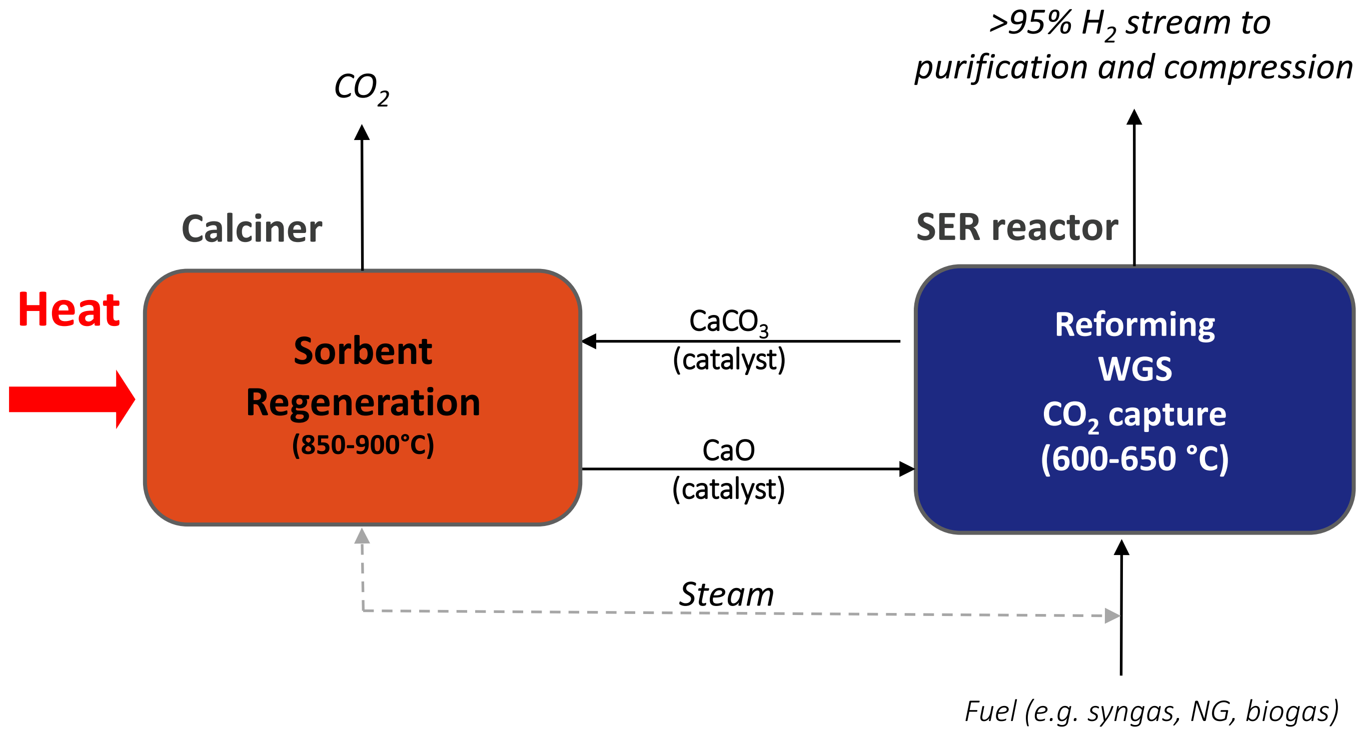


CONVERGE
CarbON Valorisation in Energy-efficient Green fuels

Sorption Enhanced reforming (SER)

SER integrates Reforming, Water-Gas Shift (WGS) and CO_2 separation through the addition of a high temperature CaO-based CO_2 solid sorbent

SER Concept scheme



Feed Gas after CCT

H2 - 41.9%

CO - 10.0%

CO2 - 32.4%

CH4 - 10.5%

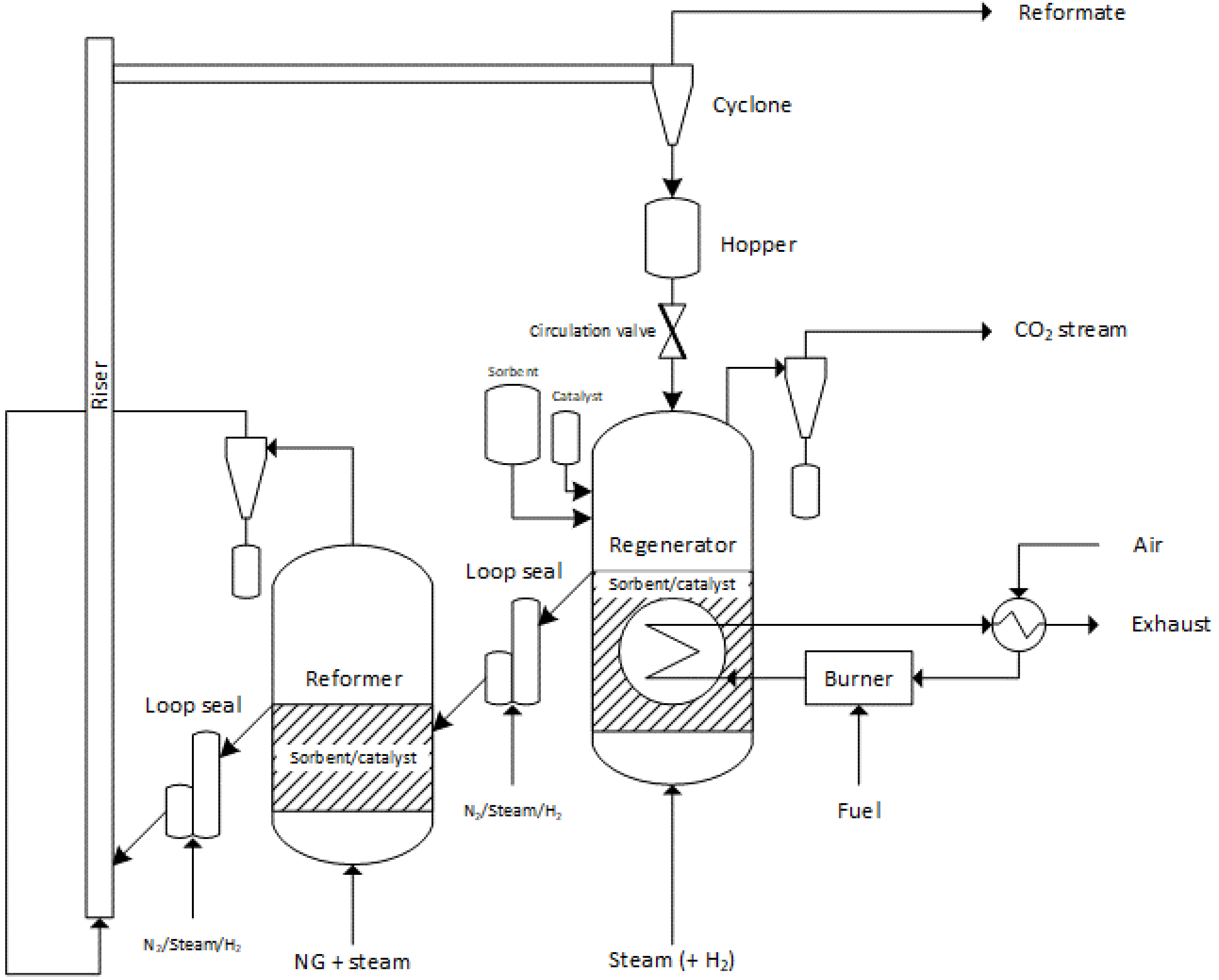
C2H4 - 4.4%

N2 - 0.9%

SER reactor technology developed at IFE

Dual Bubbling Fluidized Bed (DBFB) reactor system

- Dual bubbling fluidized bed reactor (DBFB)
  - 2 FB-reactors coupled with loop-seals and riser
  - Continuous mode
  - Bubbling regime
  - Circulation rate adjusted with slide valve

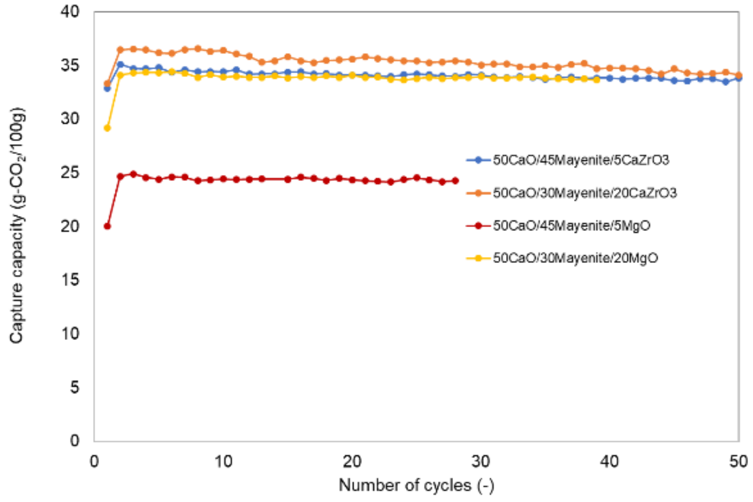


Materials Development and Optimization

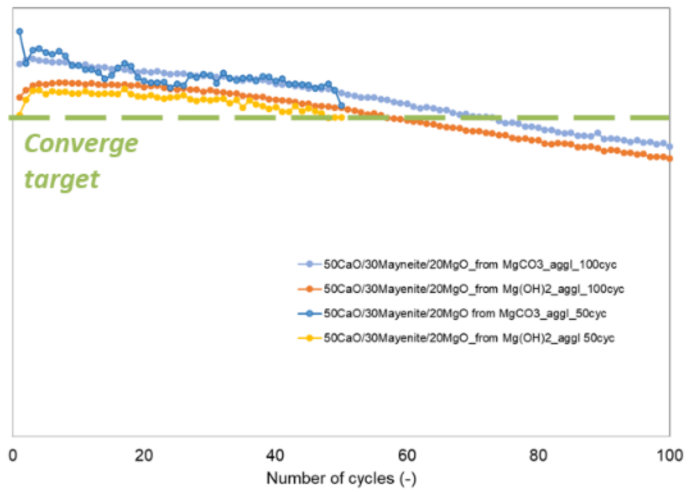
CO_2 sorbent material used in the SER process

- added a thermally stable dopant (ZrO_2, MgO and Fe_2O_3) in the CaO/Mayenite sorbent to increase its stability

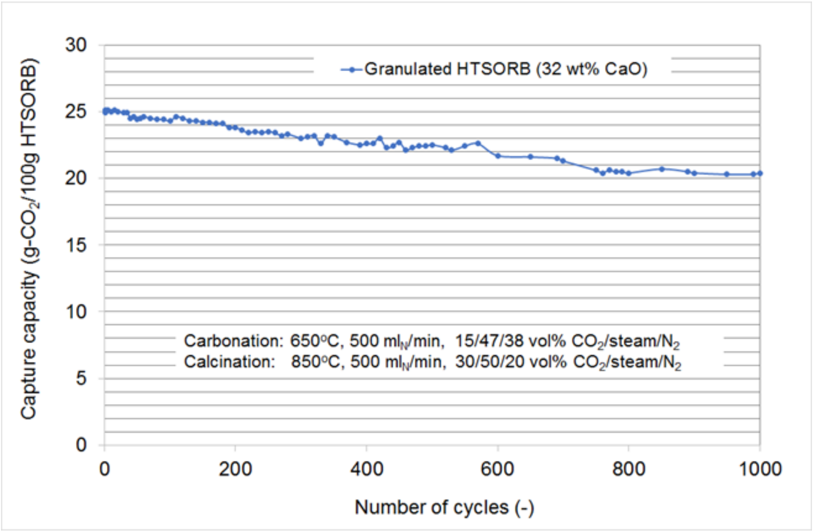
- HTSORB – Chosen for experiments



Sorbent powders: stable activity and capacity target achieved in some cases



100 cycles test: capacity decreases more severely. The addition of thermally stable agents does not allow reaching the target



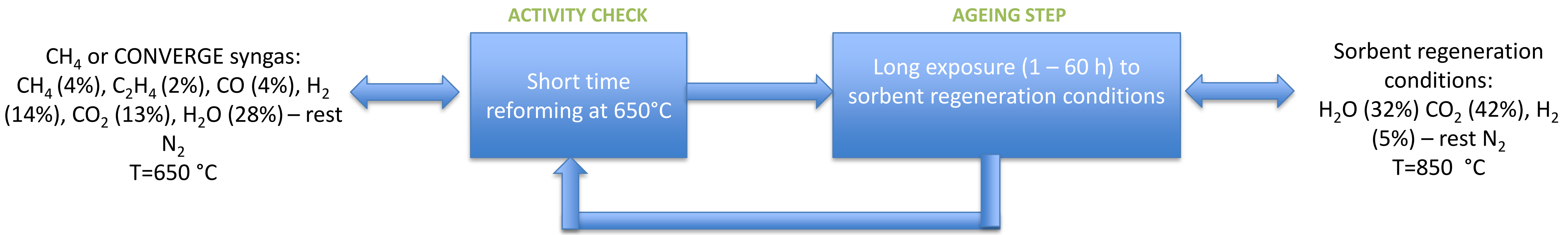
Long-term sorption capacity:
stabilized at < 20 g-CO_2/100g sorbent after 1000 carbonation-calcination cycles

Materials Development and Optimization

Development of catalyst tailored for SER process– Stability test

SER Catalyst testing and aging

- New catalytic set-up designed and constructed within CONVERGE project for “stability” and “kinetic” tests.



CONVERGE
CarbON Valorisation in Energy-efficient Green fuels

Materials Development and Optimization

Development of catalyst tailored for SER process– Stability test

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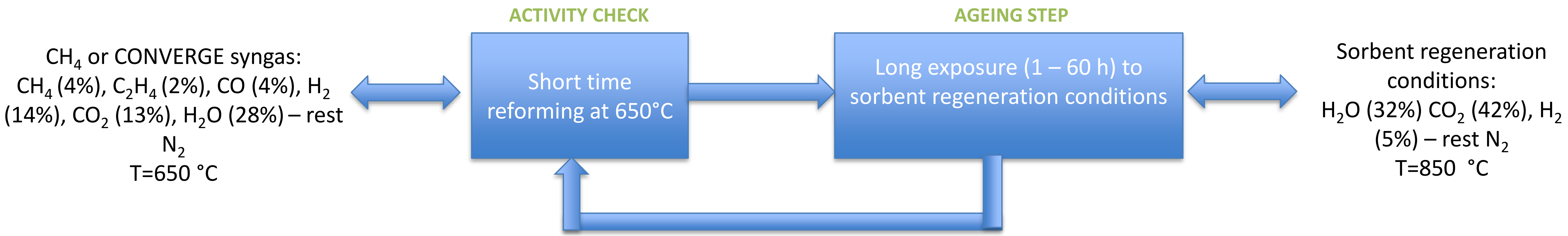


CONVERGE
CarbON Valorisation in Energy-efficient Green fuels

Materials Development and Optimization

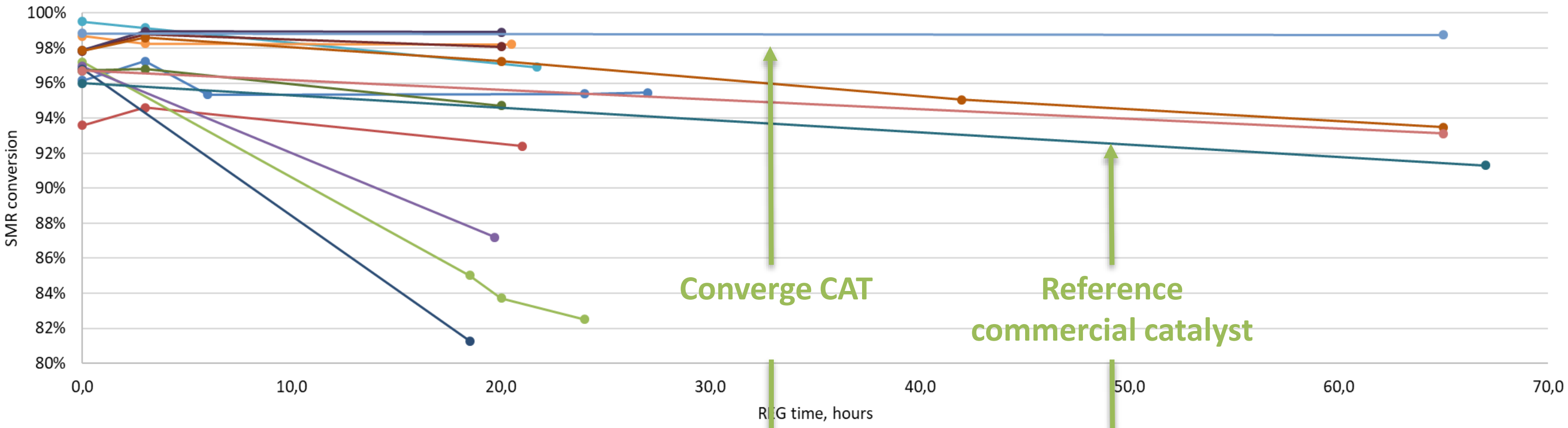
Development of catalyst tailored for SER process – Stability test

Stability tests:

Screening a matrix of 15-20 newly synthesized materials

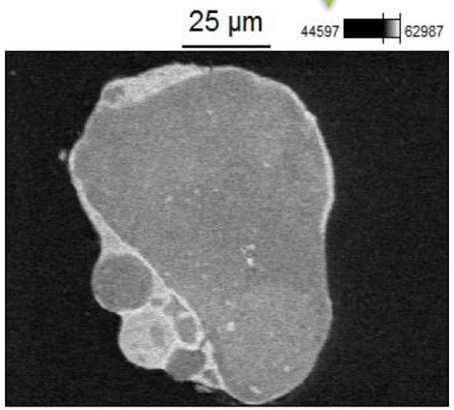
- 5 different supports
- 5-10-15-20 wt % Ni

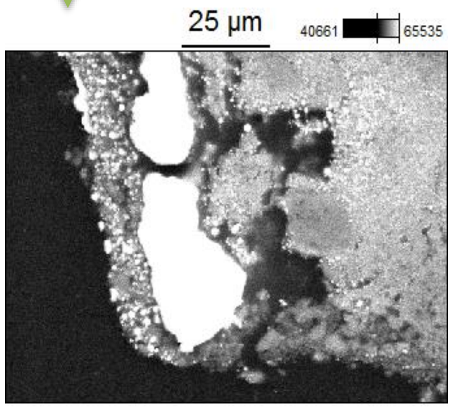
Satisfactory results, higher activity than commercial reference for some of the prepared catalysts



SEM characterization after 60h of test:

- Nickel sintering well evident in the commercial catalyst
- No evidence of nickel sintering but total nickel loading to be decreased to avoid nickel «envelop» effect

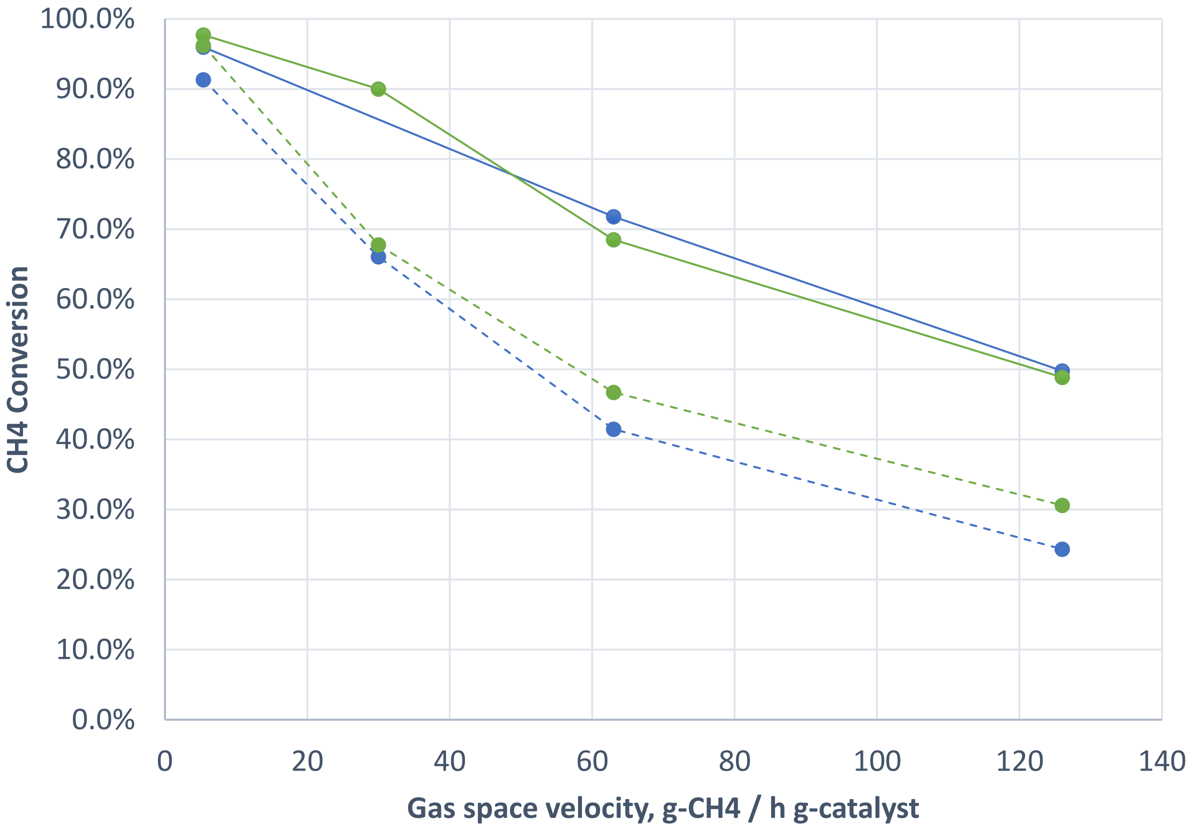




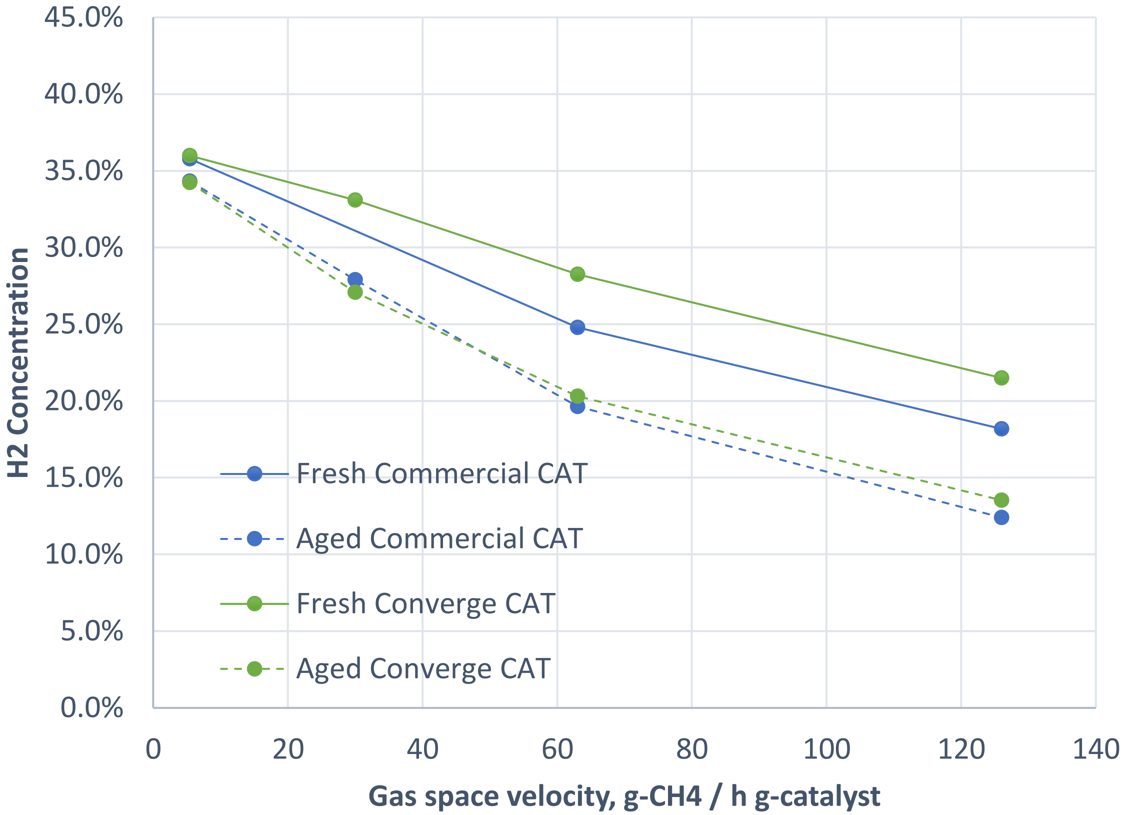
CONVERGE
CarbON Valorisation in Energy-efficient Green fuels

Materials Development and Optimization

Development of catalyst tailored for SER process– Stability test in SMR conditions (Aged 60h)



CH_4 conversion

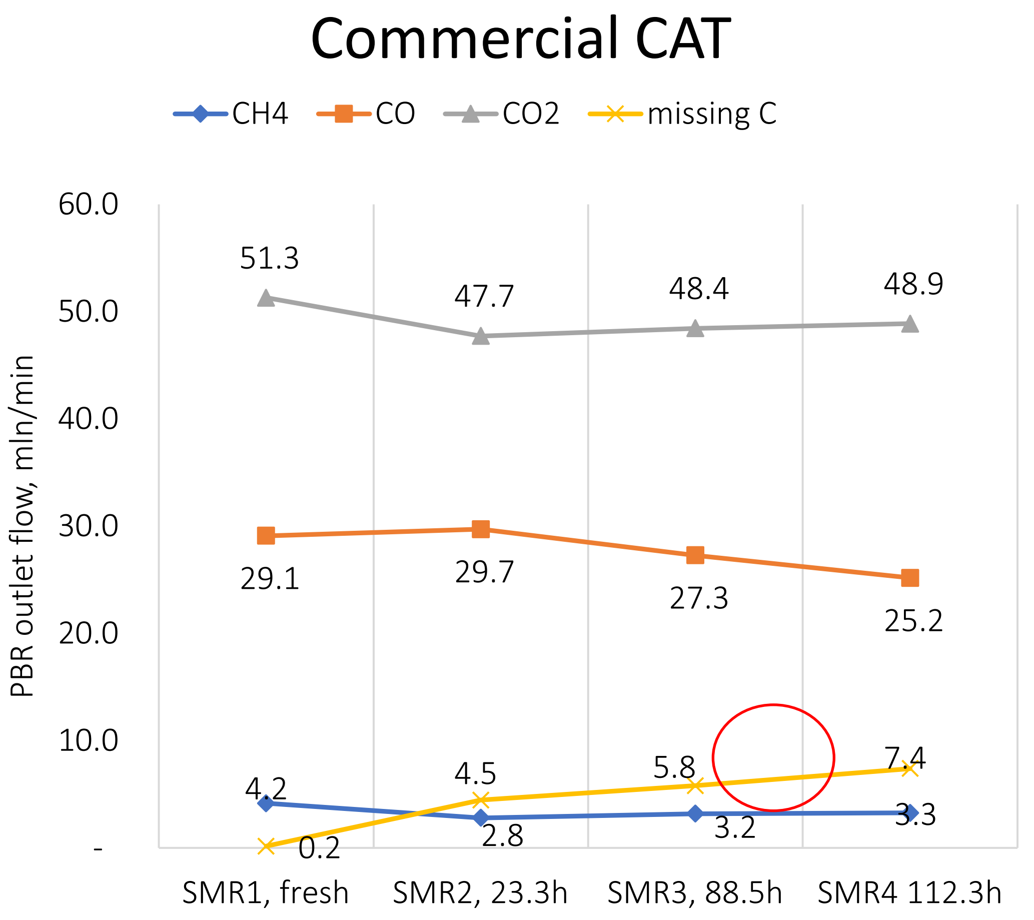


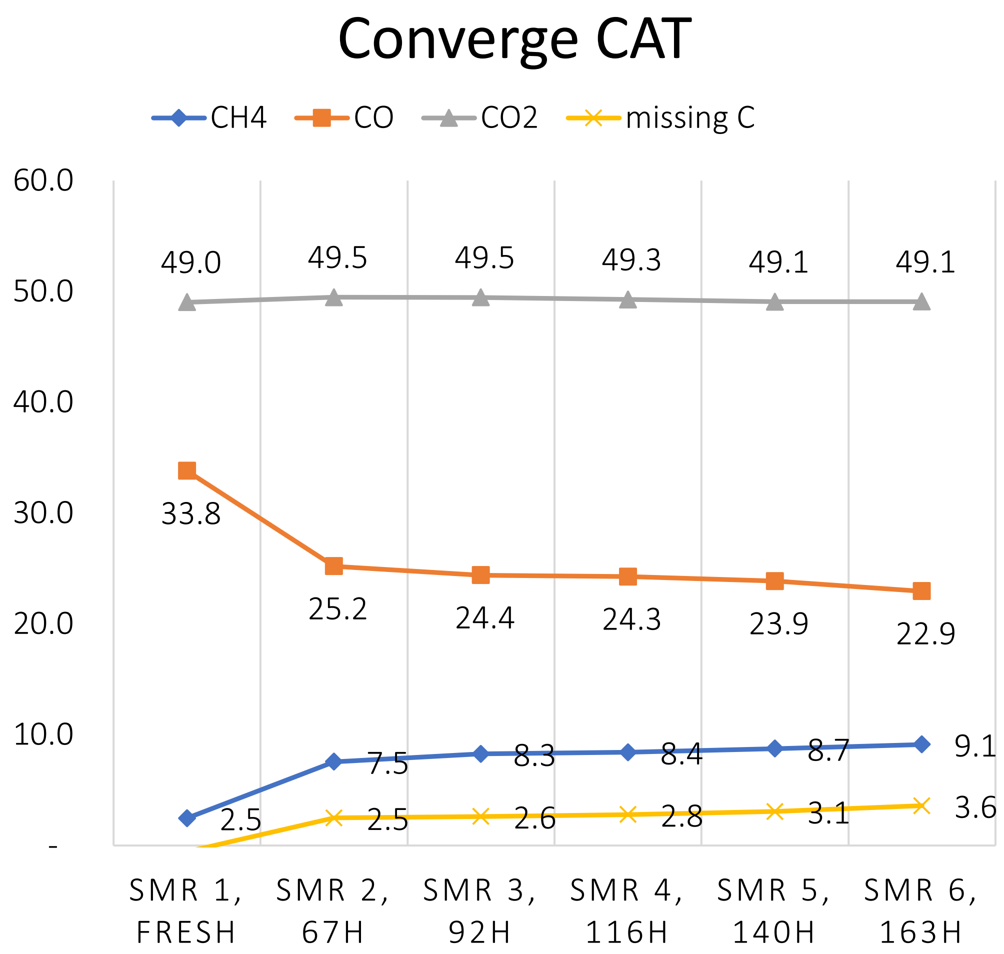
H_2 concentration

- Converge CAT presents better CH_4 conversion after aging. Difference more apparent in higher GSV.
- Converge CAT presents better H_2 selectivity fresh and after aging

Materials Development and Optimization

Development of catalyst tailored for SER process– Stability test





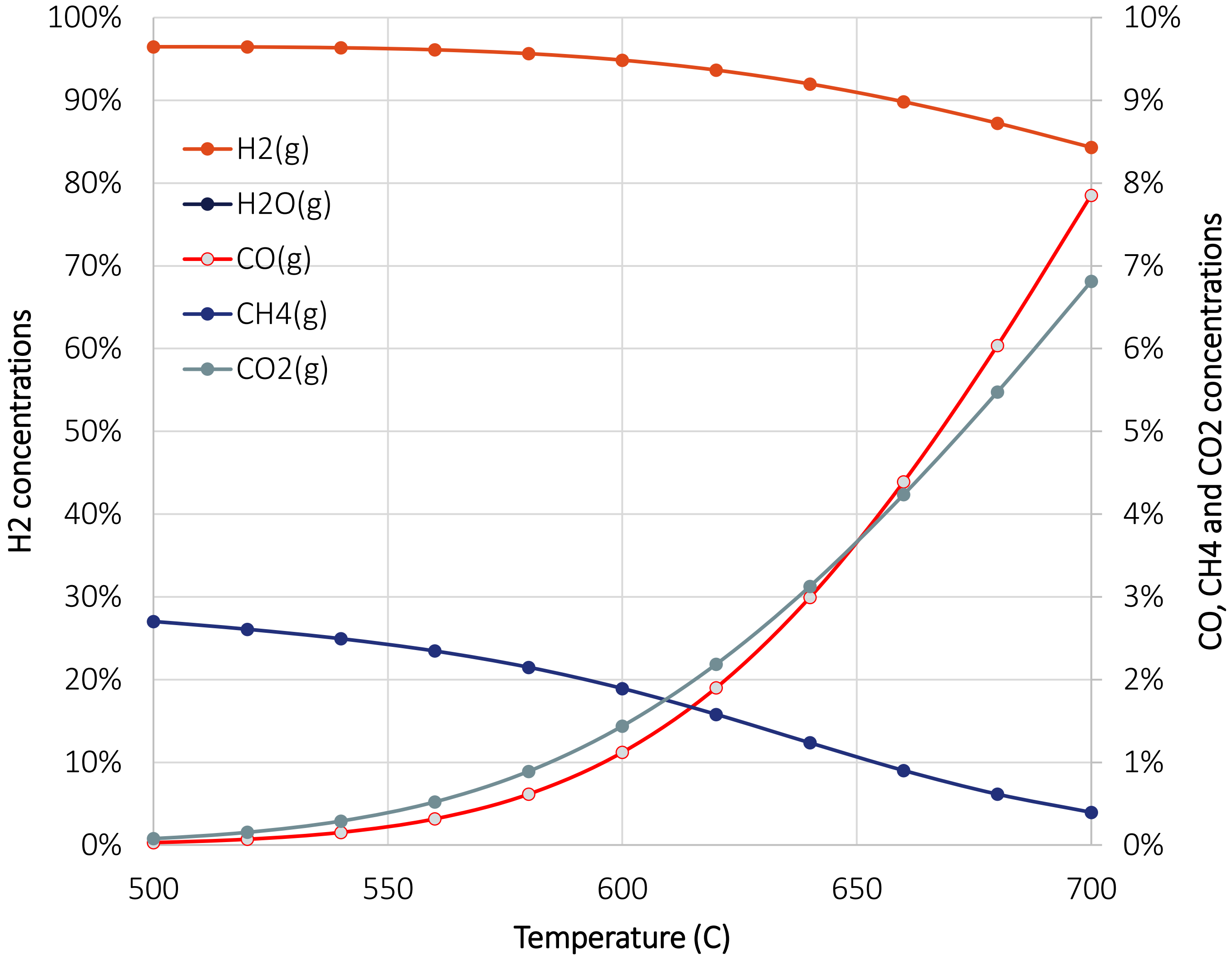
- Increase in carbon deposition. (TPO confirmed)
- Experiment stop after 120h aging – High pressure drop

- No carbon deposition
- Experiment stable during 160h aging

FBR Tests
SER/SEWGS – Equilibrium Trade-off

Process Parameters
Temperature: 650°C
Pressure: 0.5 barg
Fluidization velocity: 0.036 m/s

Feedstock and Materials
Gas Feed: (mol%): 41.9% H_2, 10.0% CO, 32.4% CO_2, 10.5% CH_4, 4.4% C_2H_4, 0.9% N_2
Steam R value: 2.0



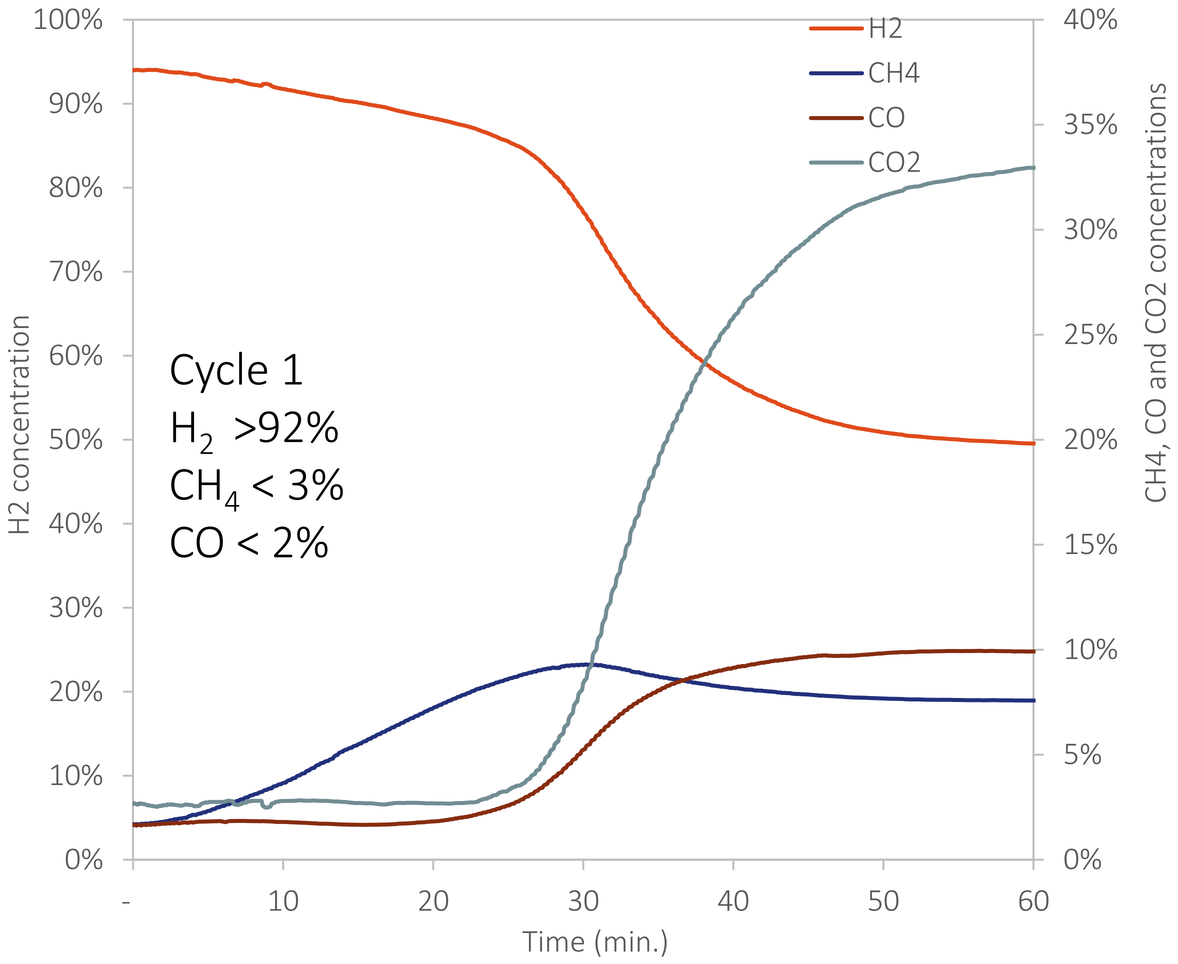
SER/SEWGS – With syngas - Converge Cat

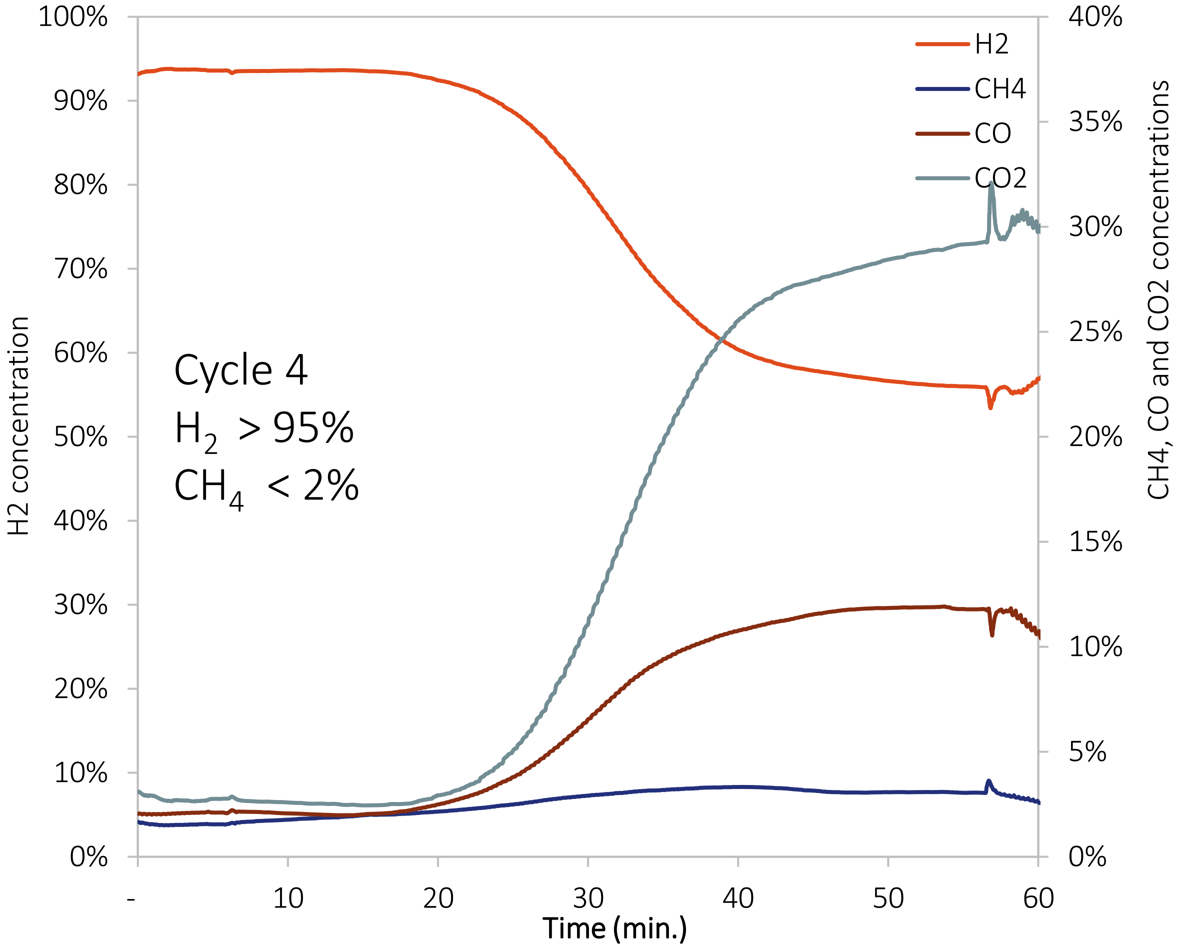
Process Parameters

Temperature: 650°C
Pressure: 0.36 barg
Fluidization velocity: 0.05 m/s

Feedstock and Materials

Gas Feed: (mol%): 41.9% H2, 10.0% CO, 32.4% CO2, 10.5% CH4, 4.4% C2H4, 0.9% N2
Steam R value: 2.0
Materials: 120.7 g CaO sorbent + 12.5 g Converge Cat

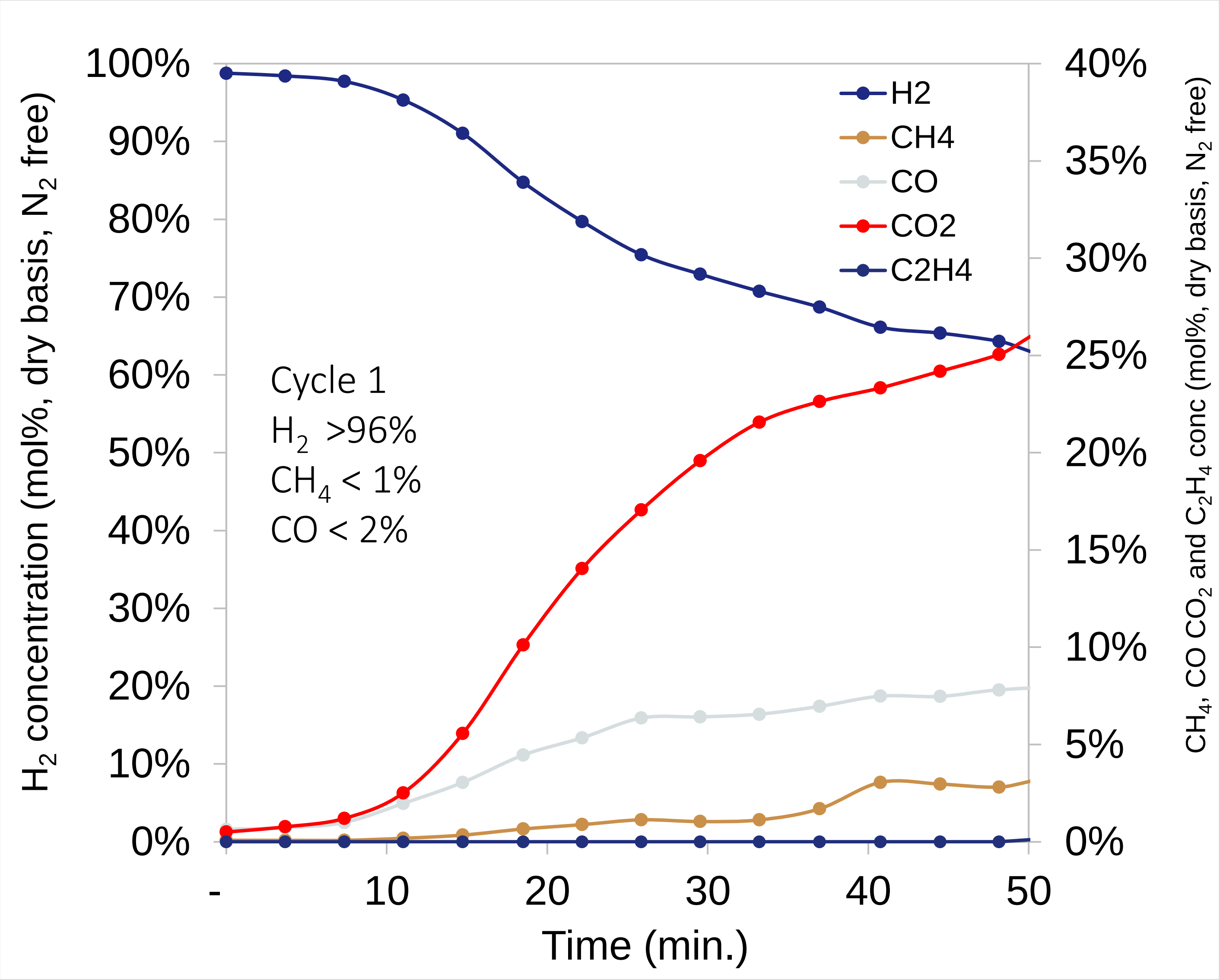




SER/SEWGS – With syngas and glycerol - Commercial Catalyst

Process Parameters
Temperature: 600°C
Pressure: 0.23 barg
Fluidization velocity: 0.053 m/s

Feedstock and Materials
Gas Feed: (mol%): 41.9% H2, 10.0% CO, 32.4% CO2, 10.5% CH4, 4.4% C2H4, 0.9% N2
Liquid Feed: glycerol 5% of gas feed
Steam R value: 2.0
Materials: 102 g CaO sorbent + 15.4 g Commercial Catalyst

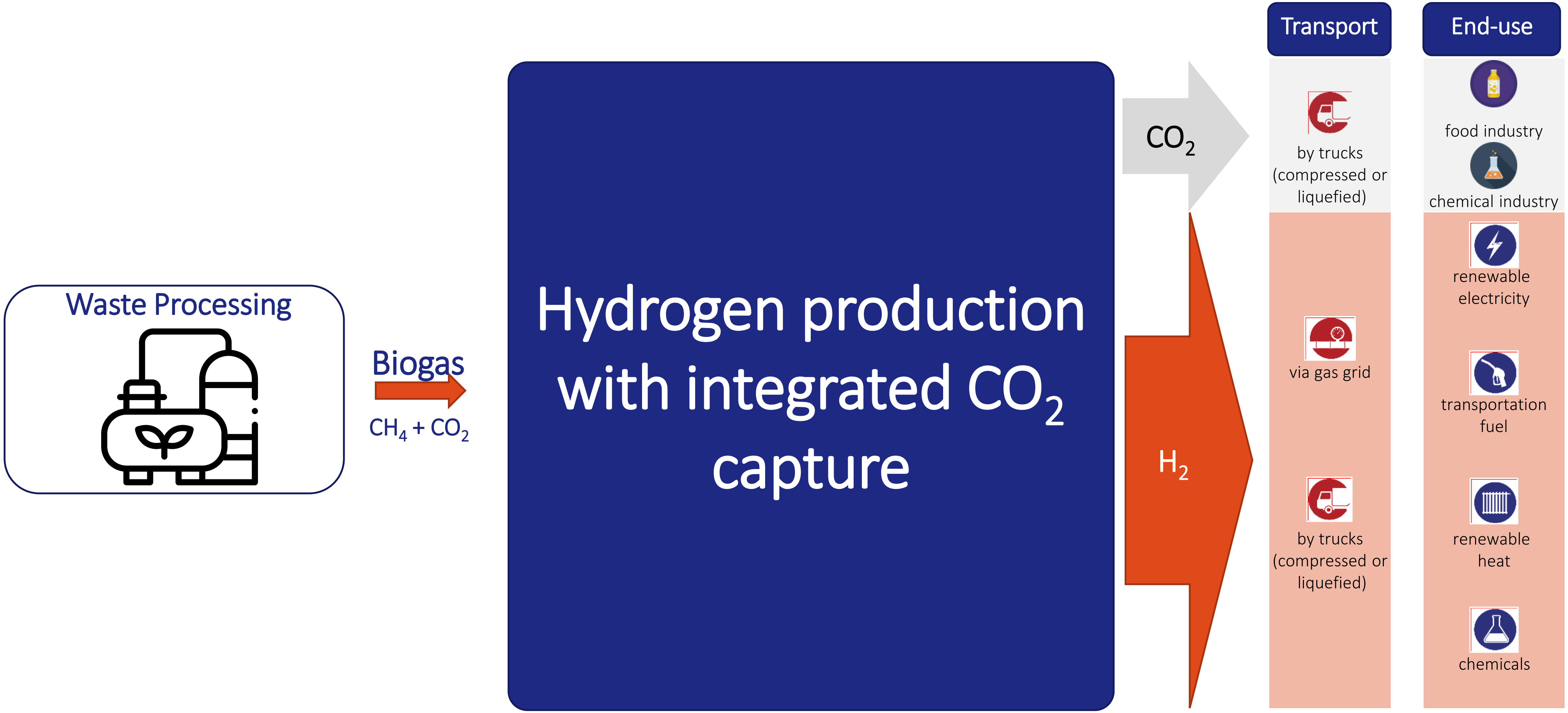


Next Steps
SER – EHC 500h demonstration at the IFE-HyNor Hydrogen Technology Center, Norway


IFE
Beyond CONVERGE

Bio4Fuels - Green Hydrogen from Biogas

Sorption Enhanced Reforming - SER

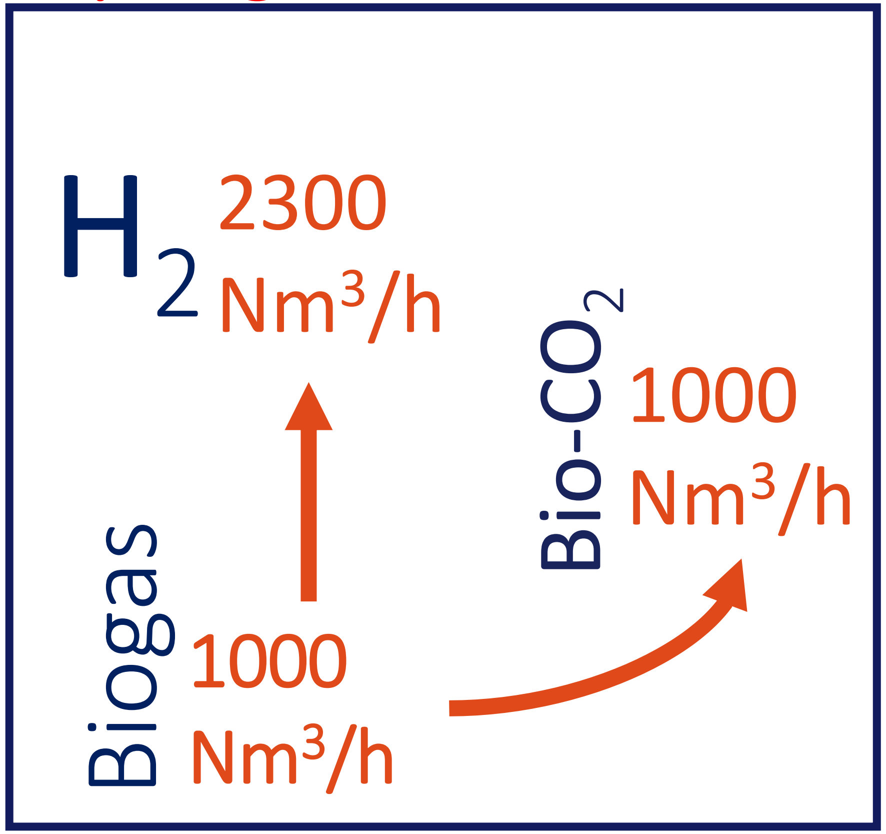


Biogas Upgrading - SER in Numbers

Conversion Efficiency

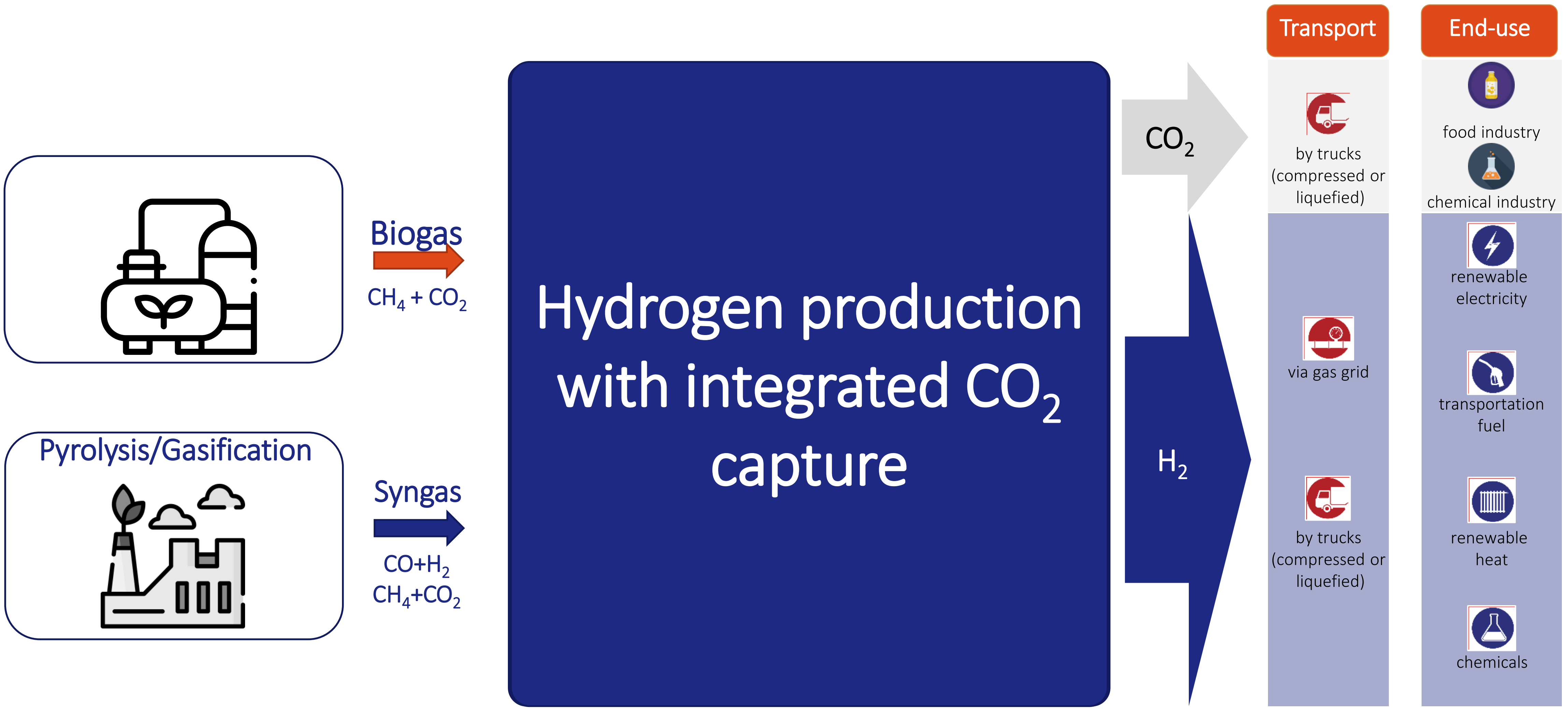
- H_2 yields (>98%) - for CH_4/CO_2 ratios varying between 1 and 2.33.
- CO_2 is over 98% pure.

Hydrogen Production



Green Hydrogen from Syngas and Biogas

Sorption Enhanced Water Gas Shift - SEWGS



Concluding Remarks

The Sorption-Enhanced Reforming/Shift technology (SER/SEWGS) allows to combine the reforming, shift and CO_2 separation in <u>two reactor vessels only</u> providing the following advantages:

- A simpler and intensified process with fewer reactors, leading to a potentially more compact system
- Fewer costly consumables (no shift catalysts, no CO_2 solvent + additives)
- Improved heat integration possibilities due to CO_2 removal at high temperature
- Separated H_2 (>95 vol%) and CO_2 (> 95 vol%) streams that can be recombined for different fuel/chemical synthesis (methanol, DME) or valorised separately for other markets.
- The excess CO_2 can be sequestrated (BECCS), used to substitute fossil CO_2 in industrial applications or as chemical, or combined with renewable H_2 to produce electro-fuels in power-to-X concepts for energy storage.
- The produced H_2 can also be used alone, as chemical or as fuel.
- Can reform liquid such as glycerol

- **These advantages result in CAPEX reduction of about 20-30% compared to conventional commercially available technologies.**

The CONVERGE project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 818135

Website: www.converge-h2020.eu
Researchgate: **CONVERGE: CarbON Valorisation in Energy-efficient Green fuels**
Linkedin: **showcase/converge-horizon2020**

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CO_2 direct hydrogenation to DME via membrane reactor

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[1]Inorganic membranes and membrane reactors, Eindhoven University of Technology.
[2]TECNALIA, Basque Research and Technology Alliance (BRTA)

International workshop on CO_2 capture and utilization
16th and 17th February 2021

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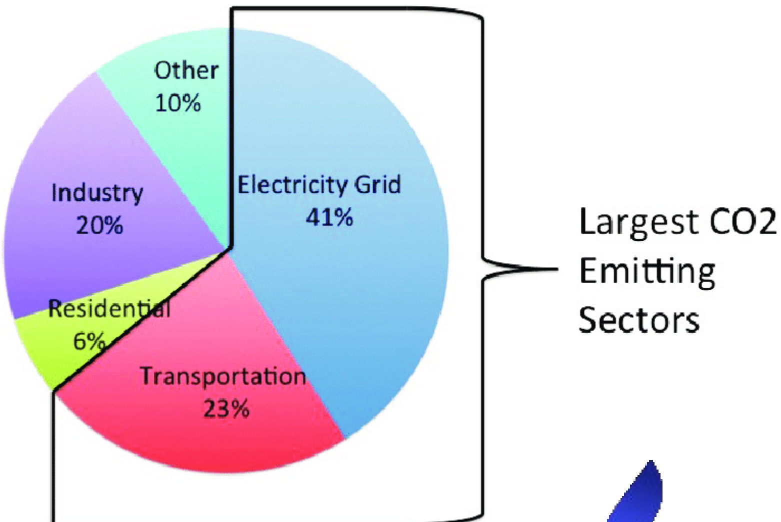
C2FUEL project – Agreement N°83014 - confidential

Introduction

CO_2 emissions and possible solution

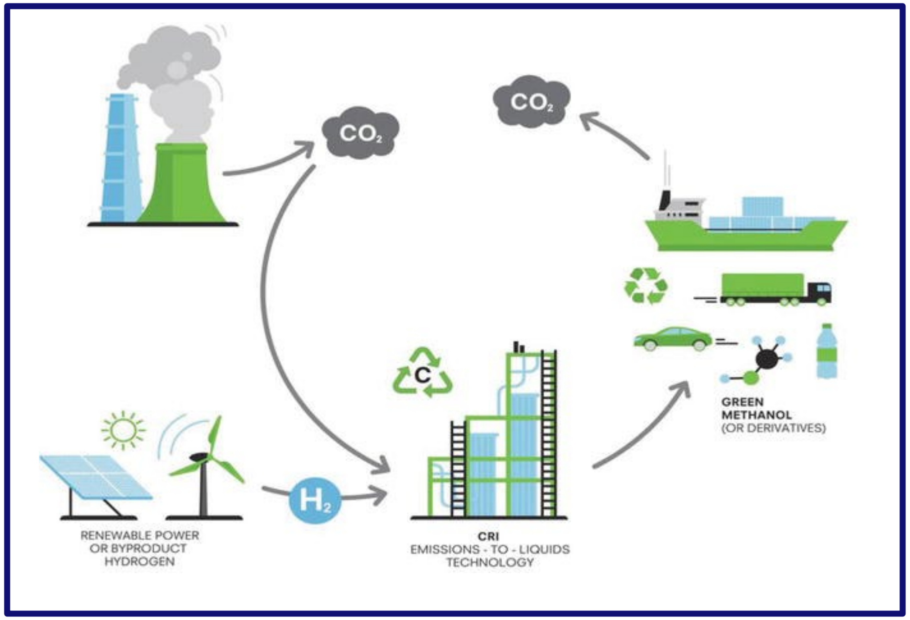
CO_2 emission per sector

Source: IEA (2017)



How to reduce emissions?

CO_2 capture and reconversion



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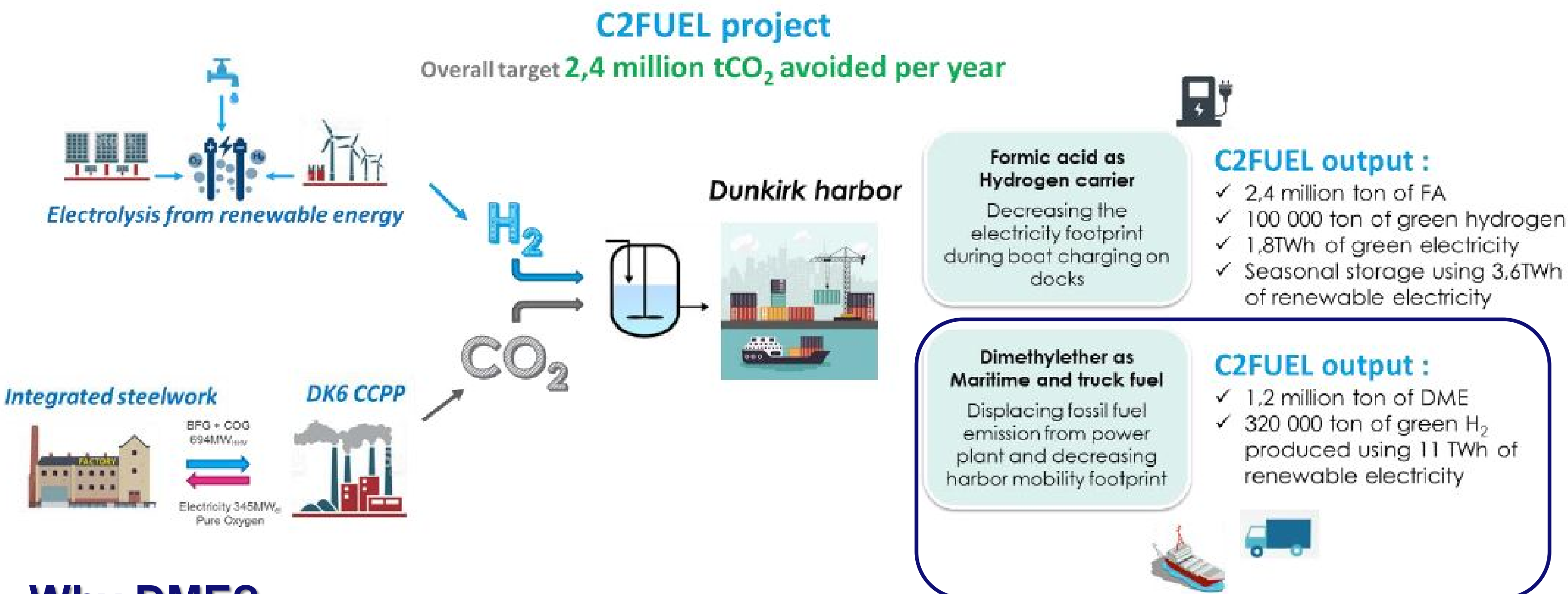
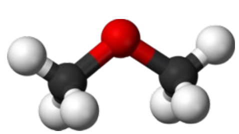
Introduction

CO_2 emissions and possible solution



Why DME?



Chemical and physical properties similar to LPG

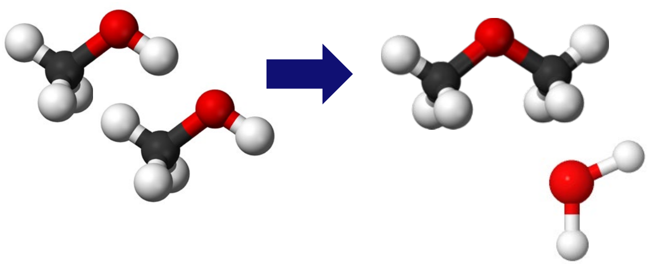
↓

Good candidate as transportation fuel

Development and upscale of DME production from CO_2

Introduction

DME production



Indirect route

Methanol synthesis over a Cu-ZnO-Al_2O_3 catalyst

Methanol dehydration to DME over an acid catalyst (HZSM-5)

Direct route

DME synthesis over a Cu-ZnO-Al_2O_3/HZSM-5 bifunctional catalyst

- ☑ One reactor
- ☑ Less limited by thermodynamics
- ☒ More difficult separation

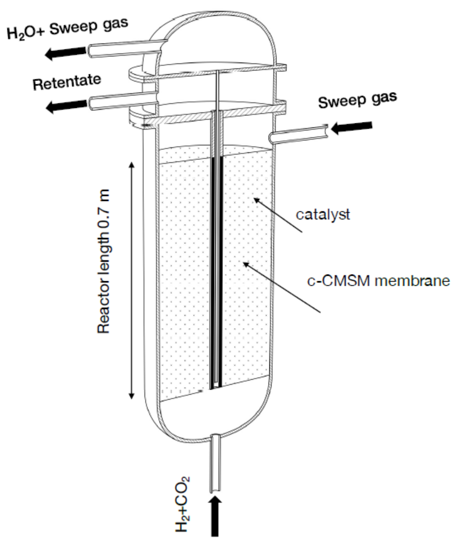
Nowadays the main source is syngas →

- Syngas production causes CO_2 emissions
- Depending on syngas composition, CO_2 can be produced

Direct DME synthesis from CO_2

1. CO_2 hydrogenation: $CO_2 + 3H_2 \rightleftarrows CH_3OH + \cancel{H_2O}$ ΔH_0 = -49.5 kJ/mol
2. Reverse WGS: $CO_2 + H_2 \rightleftarrows CO + \cancel{H_2O}$ ΔH_0 = 41.2 kJ/mol
3. Methanol dehydration: $2CH_3OH \rightleftarrows CH_3OCH_3 + \cancel{H_2O}$ ΔH_0 = -23.4 kJ/mol

Process conditions	200-250 ºC - 20-50 bar



Membrane reactor

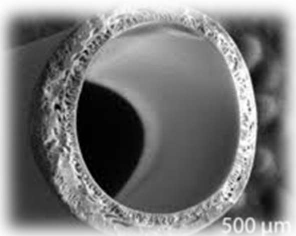
Membrane for selective water removal

- ☑ Reaction and separation in the same unit
- ☑ Overcome thermodynamic limitations
- ☑ Avoid catalyst deactivation due to water adsorption

Membrane requirements:

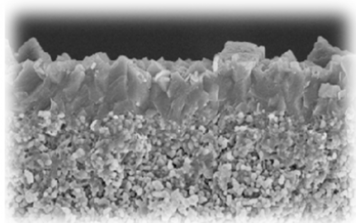
Hydrophilicity + Stability (thermal, mechanical, chemical) + High vapor/gas selectivity

Polymeric membranes



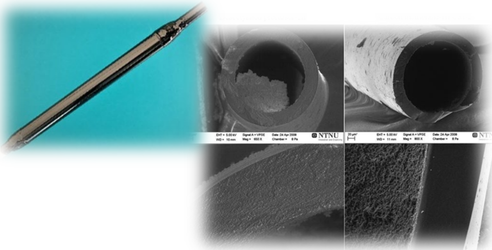
- High permeability
- Low stability (thermal-mechanical)

Ceramic membranes
(zeolite, alumina, etc.)



- High permeability/selectivity
- Low stability (hot humid environment)

Carbon membranes



- Possible hydrophilicity
- Stability
- Possibility to tune properties

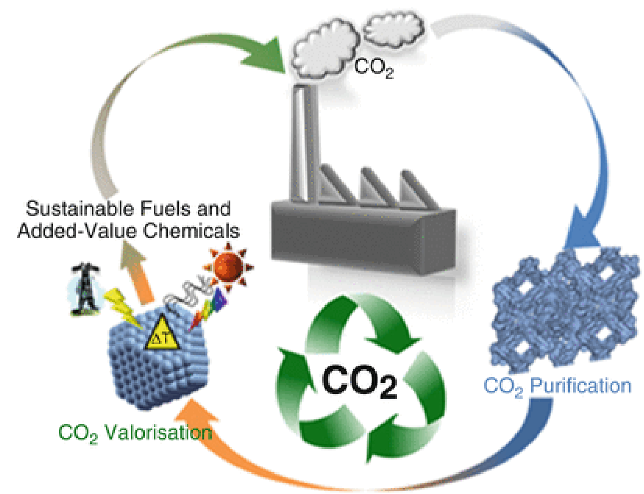
Introduction

Project goals:

1. Development of carbon membranes (TECNALIA & TU/e)
   - Synthesis of Al-CMSM with improved hydrophilicity
   - Characterization of Al-CMSM
2. Development of a 1D-phenomenological membrane reactor model (TU/e)
   - Effect of membrane properties on reactor performance
   - Optimize the operating conditions
   - Propose a cooling strategy

Main objective:

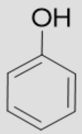
Promote a valid alternative for CO_2 valorization



Development of Al-supported Carbon Molecular Sieve Membranes

Carbon molecular sieve membranes

Development and manufacturing Al-CMSM



Phenol

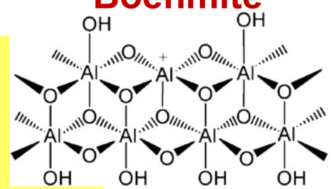
+ $CH_2{=}O$

Formaldehyde

Phenolic resins

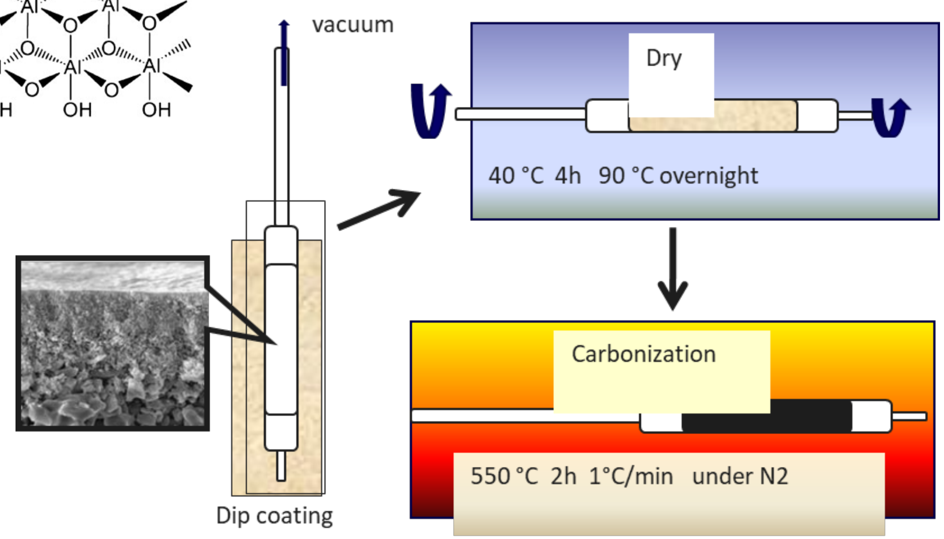
Novolac : acidic media and Formaldehyde /Phenol ≈ 0.75-0.85

Boehmite



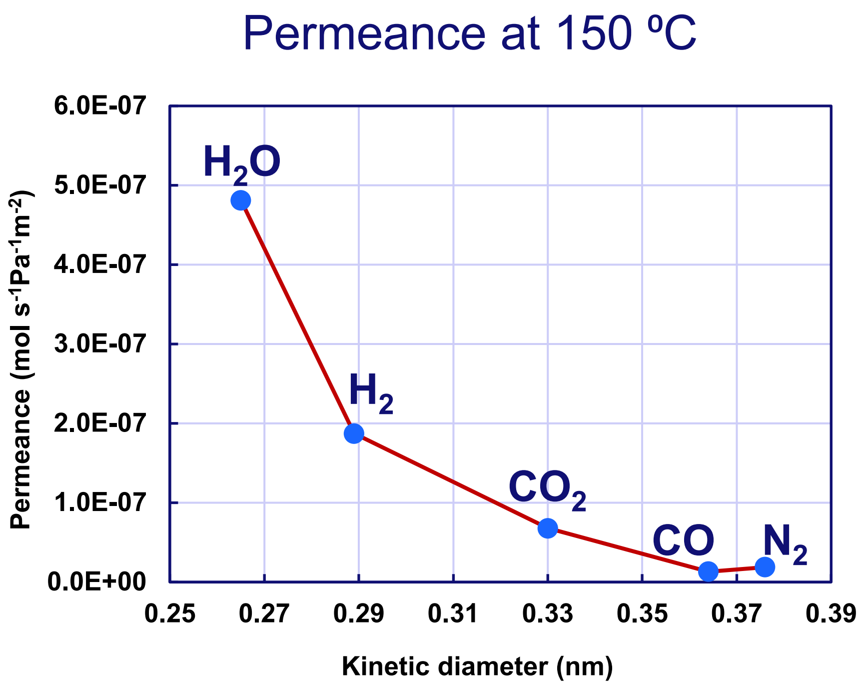
Dipping solution

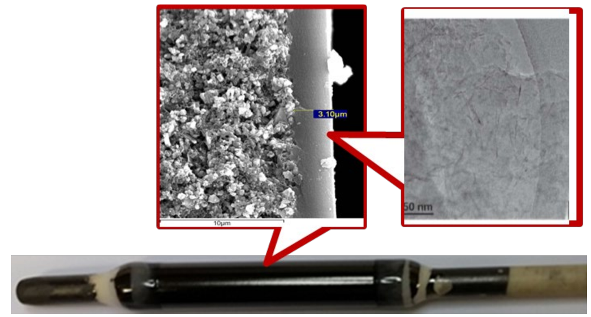
Boehmite nanoparticles	**0,8 %**
Novolac resin	13,0 %
Formaldehyde	2,0 %
Ethylenediamine	0,6 %
Solvent	NMP

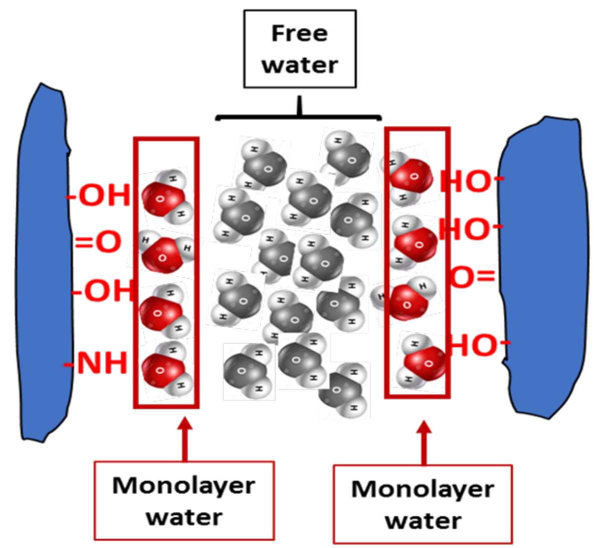


Carbon molecular sieve membranes

Development and manufacturing Al-CMSM





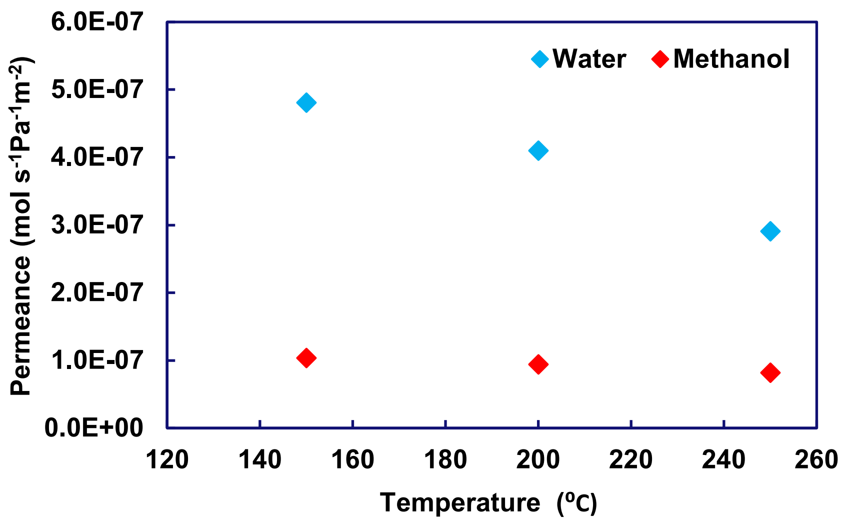


Carbon molecular sieve membranes

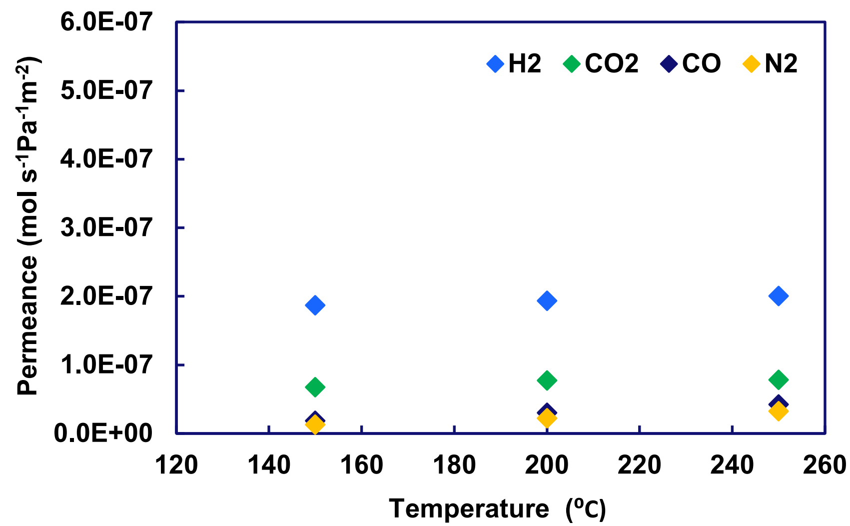
Development and manufacturing Al-CMSM

Single gas-vapor permeation experiment at ΔP = 3 bar

Vapor permeation



Gas permeation



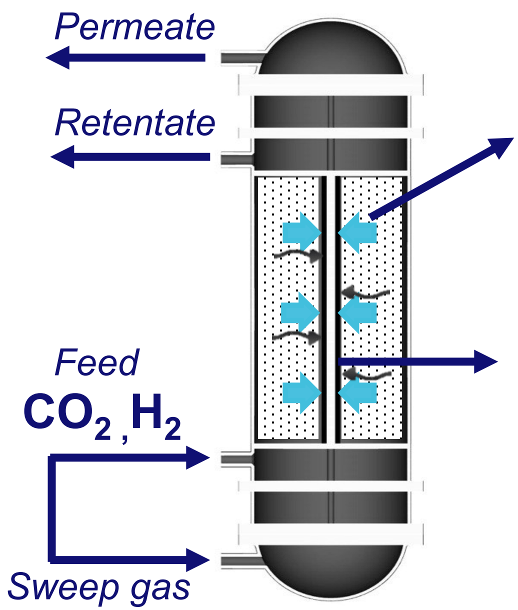
Water has the highest permeance at each condition

Membrane reactor model for the CO_2 hydrogenation to DME

Membrane reactor model

Reactor features and model hypotheses:

Fixed bed membrane reactor



Reaction zone
Bifunctional catalyst bed:
$CuZnOAl_2O_3$/HZSM-5

Permeation zone
Hydrophilic Membrane

Trans-membrane flux :

$$J_i = \wp_i \cdot \left(P_i^R - P_i^P \right)$$

Sweep gas (CO_2+H_2)

Water removal   Heat removal

Co-current configuration

Model equations → Mass balances + Energy balances + Momentum balance

- *Reaction*
- *Permeation*

- *Reaction (Ergun)*
- *Permeation (No P drops)*

Membrane reactor model

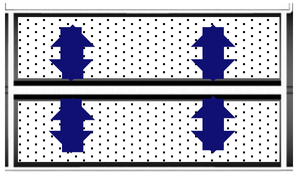
Model equations and approach:

Reactor performances

$$X_{CO_2} = \frac{F^R_{CO_2 0} - F^R_{CO_2} + F_{CO_2,tmb}}{F^R_{CO_2,0} + F^*_{CO_2,tmb}}$$

$\underline{CO_2\ transmembrane\ flow}$

$$F_{CO_2,tmb} = F^P_{CO_2,0} - F^P_{CO_2}$$



$$F^*_{CO_2,tmb} = 0 \quad \text{if } F_{CO_2,tmb} \leq 0 \quad Reactant\ loss$$

$$F^*_{CO_2,tmb} = F_{CO_2,tmb} \quad \text{if } F_{CO_2,tmb} > 0 \quad Reactant\ cofeeding$$

$$Y_i = \frac{N_{c,i}\left(F^R_i + F^P_i\right)}{F^R_{CO_2,0} + F^*_{CO_2,tmb}}$$

$$WR = \frac{F^P_{H_2O}}{F^P_{H_2O} + F^R_{H_2O}} \longrightarrow$$ Amount of water removal

1. Assessment of the membrane optimal properties (permeability and selectivity) ➡ **Isothermal conditions**
2. Optimization of the operating conditions ➡ **Sweep gas for heat management**

T^R_{in} T^P_{in} $\boxed{\begin{array}{l}\Delta P = P^R - P^P \\ SW = F^P_{in}/F^R_{in}\end{array}}$ $H_2\colon CO_2$

Influencing the driving force for permeation

$\boxed{\begin{array}{l}P^R_{in} = 40\ bar \\ T^R_{avg} = 200°\mathrm{C}\end{array}}$

Fixed conditions

Membrane reactor model

Assessment of the membrane optimal properties:

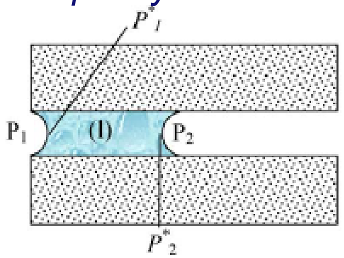
Definitions:

Permeance $\wp_i \quad [mol/(Pa \cdot m^2 \cdot s)]$

Selectivity $S_{H_2O,i} = \wp_{H_2O}/\wp_i$

Main mechanism of water and methanol permeation:

Capillary condensation



Main mechanism of gases permeation:

Molecular sieving

Kinetic diameters

$H_2 < CO_2 \approx CO < DME$

Procedure:

Ideal membrane → Real membrane

H_2O and H_2 permeating → All the species permeating

Hypotheses:

1. CO_2 and CO same permeance
2. H_2O/ CH_3OH selectivity ≥1 (slightly)
3. DME is not permeating (largest size and Tc=128℃)

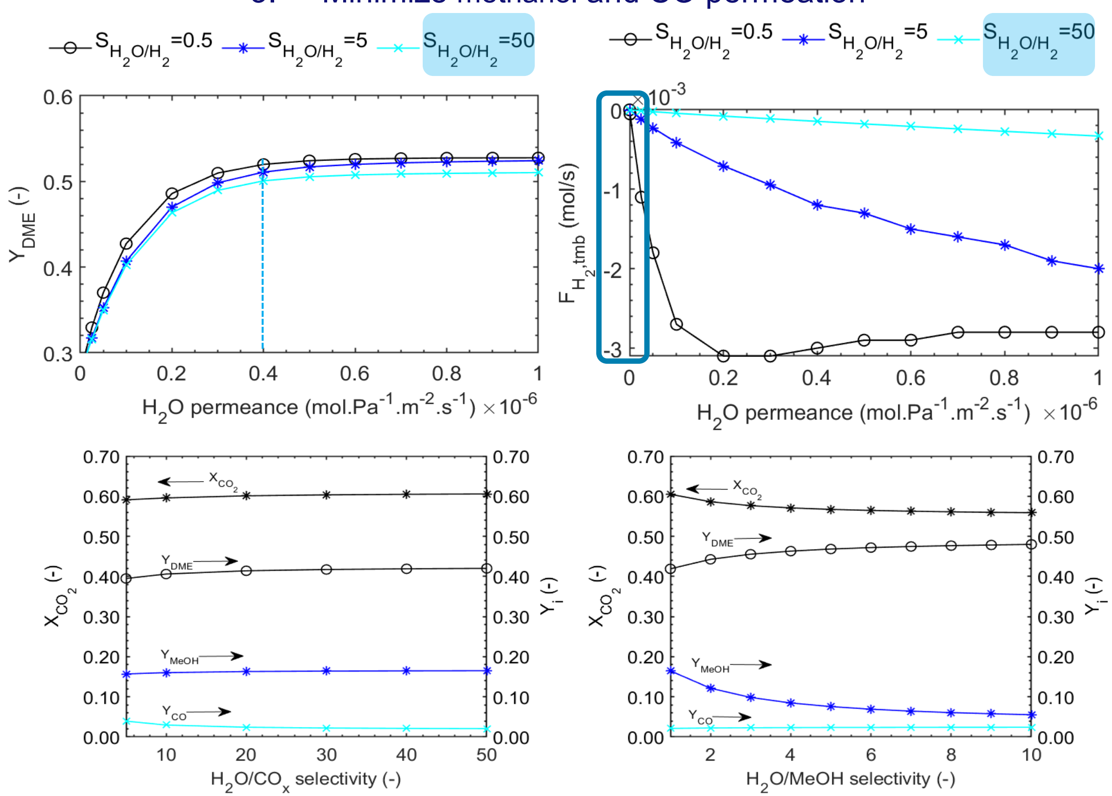
Operating conditions			
T^R and T^P	200°C	SW	3
P^R	$40\ bar$	H_2:CO_2	3
ΔP	$0\ bar$	$\Phi^R_{H_2,0}$	$1\ Nm^3/h$

Assessment of the membrane optimal properties:

According to the assumption made + Criteria used

1. Maximize water permeation flow
2. Minimize loss and co-feeding of reactants
3. Minimize methanol and CO permeation

Membrane optimal properties	
$\wp_{H_2O}$ (mol/(Pa · m² · s))	$4 \cdot 10^{-7}$
S_{H_2O/H_2}	50
S_{H_2O/CO_2}	30
$S_{H_2O/CO}$	30
S_{H_2O/CH_3OH}	10
$S_{H_2O/DME}$	∞



Good agreement with:

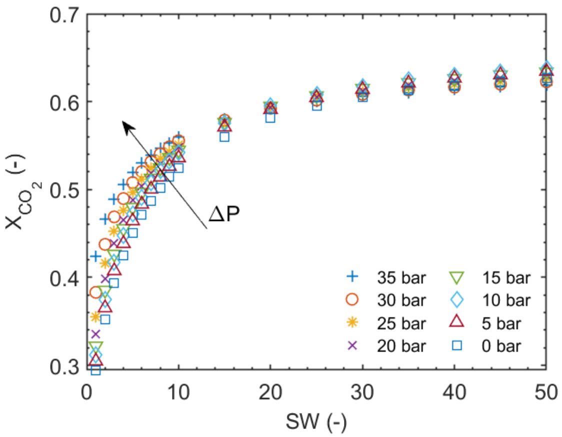
- ceramic membranes
- polymeric membranes

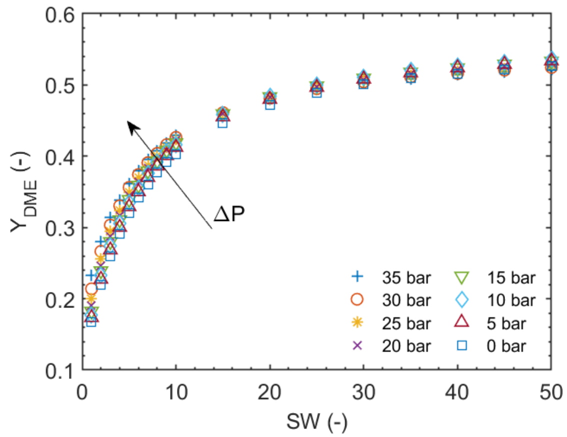
Not enough data available for carbon membranes

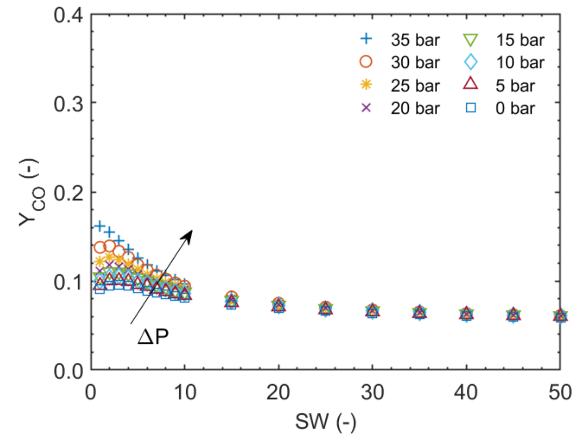
Membrane reactor model

Optimization of the operating conditions:

Effect of SW and ΔP on reaction performance

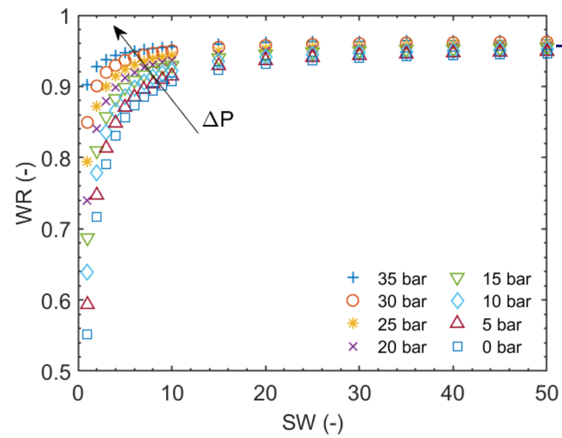






↑ **SW** **More efficient water removal**

↑ **ΔP** **No significant effect *(especially at higher SW)***



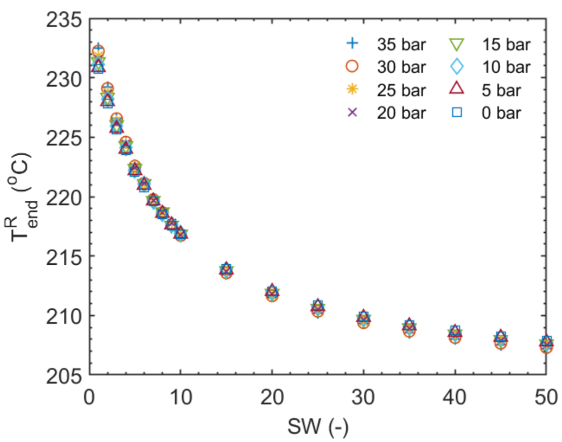
High efficiency of water separation

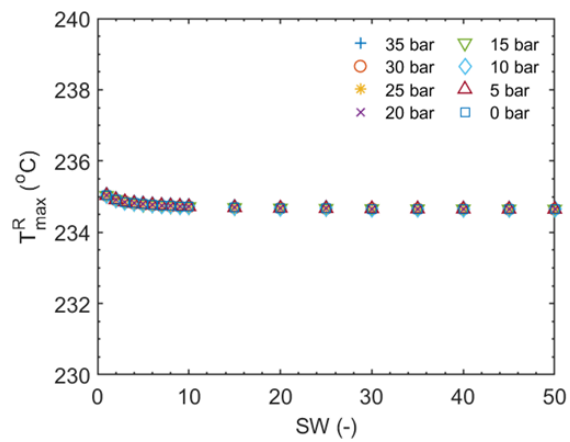
WR≈96%

Membrane reactor model

Optimization of the operating conditions:

Effect of SW and ΔP on heat management





↑ **SW** **More heat removal**

↑ **ΔP** **No significant effect** ***(especially at higher SW)***

T-profile optimization criteria:

- T lower than 270-300℃ (catalyst deactivation due to sintering)
- As low as possible (desired reactions: exothermic, undesired reactions: endothermic)
- Lower T guarantees higher water permeation and lower gas permeation
- Higher than 190-200 ℃ (catalyst activation temperature)

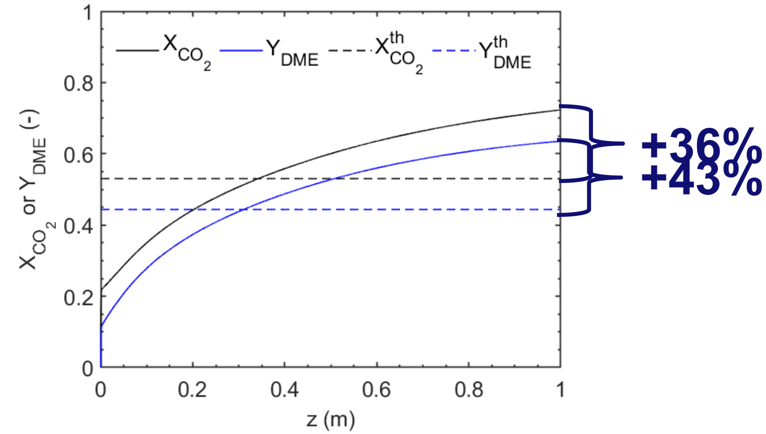
$$T_{in}^{P} = 185\ ^{0}C \qquad T_{in}^{R} = 200\ ^{0}C \qquad SW = 20 \qquad \Delta P = 5\ \text{bar}$$

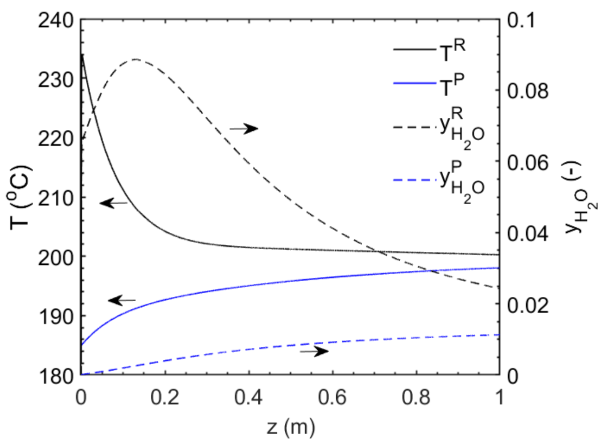
Optimize heat & water removal

Membrane reactor model

Membrane reactor optimal performance:

Optimal conditions		Fixed conditions	
SW	20	$\Phi^R_{H_2,0}$	$1\ Nm^3/h$
ΔP	5 bar	P^R_{in}	40 bar
H_2:CO_2	3.5	T^R_{in}	200 ℃
T^P_{in}	185 ℃		





- Temperature and water concentration show similar profiles
- The efficiency of water removal is 96%

Conclusions

1. The **Al-CMSM** showed high water permeance and vapor/gas selectivity

2. There is no need to have the highest **membrane performance**.
   An optimum has been found for water permeance and selectivity.

3. The **sweep gas** promotes both **heat** and **water removal**.
   The temperature profile can be optimized thanks to the sweep gas inlet temperature

4. The **cocurrent configuration** has several positive effects:
   - Highest driving force for heat and water removal is at the entrance
   - Water back permeation is avoided

5. The operating conditions have been optimized. Considerations are:
   - There is no need to have a high ΔP
   - A sweep gas is used instead, with a higher flow rate. The sweep gas can be recirculated.

6. The **thermodynamic limitations** have been overcome
   (with a 96% efficiency of water removal)

Any question?

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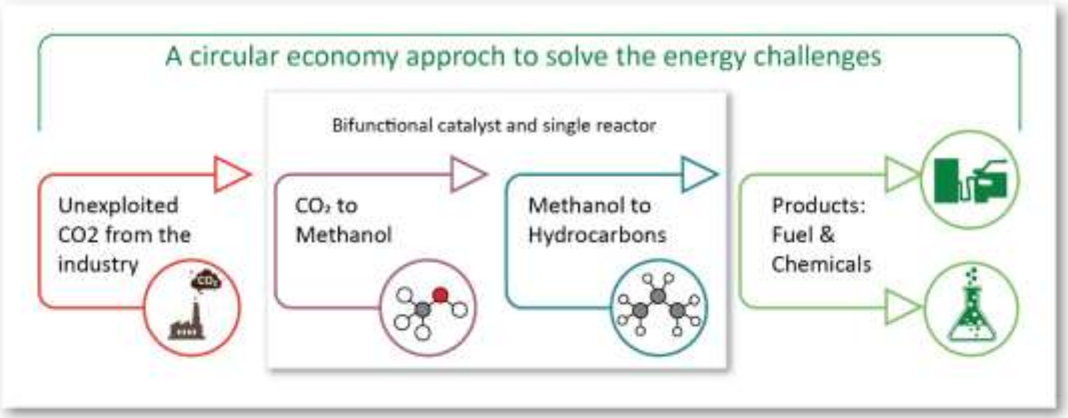
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 838014 (*C2Fuel* project).

CO2MOS

Efficient CO_2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS



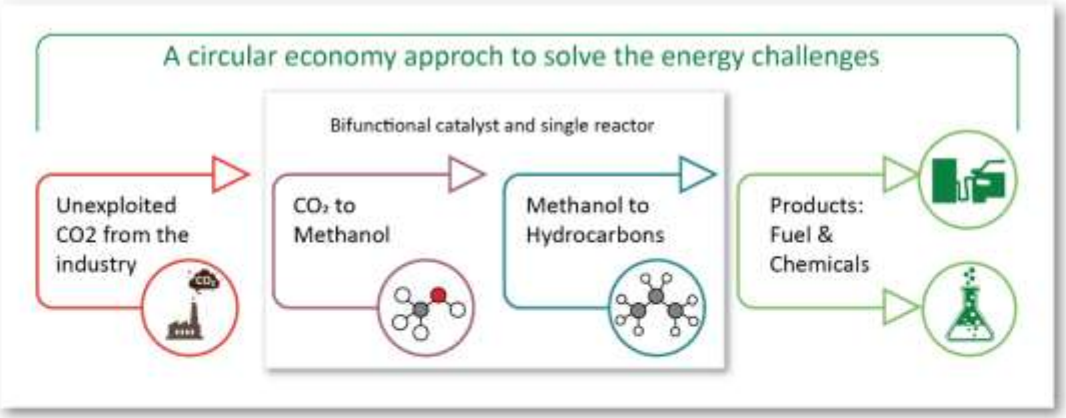
Catalyst development within the COZMOS project

Unni Olsbye, University of Oslo

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

CO2MOS

Efficient CO_2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS



Catalyst development within the COZMOS project

Unni Olsbye, University of Oslo

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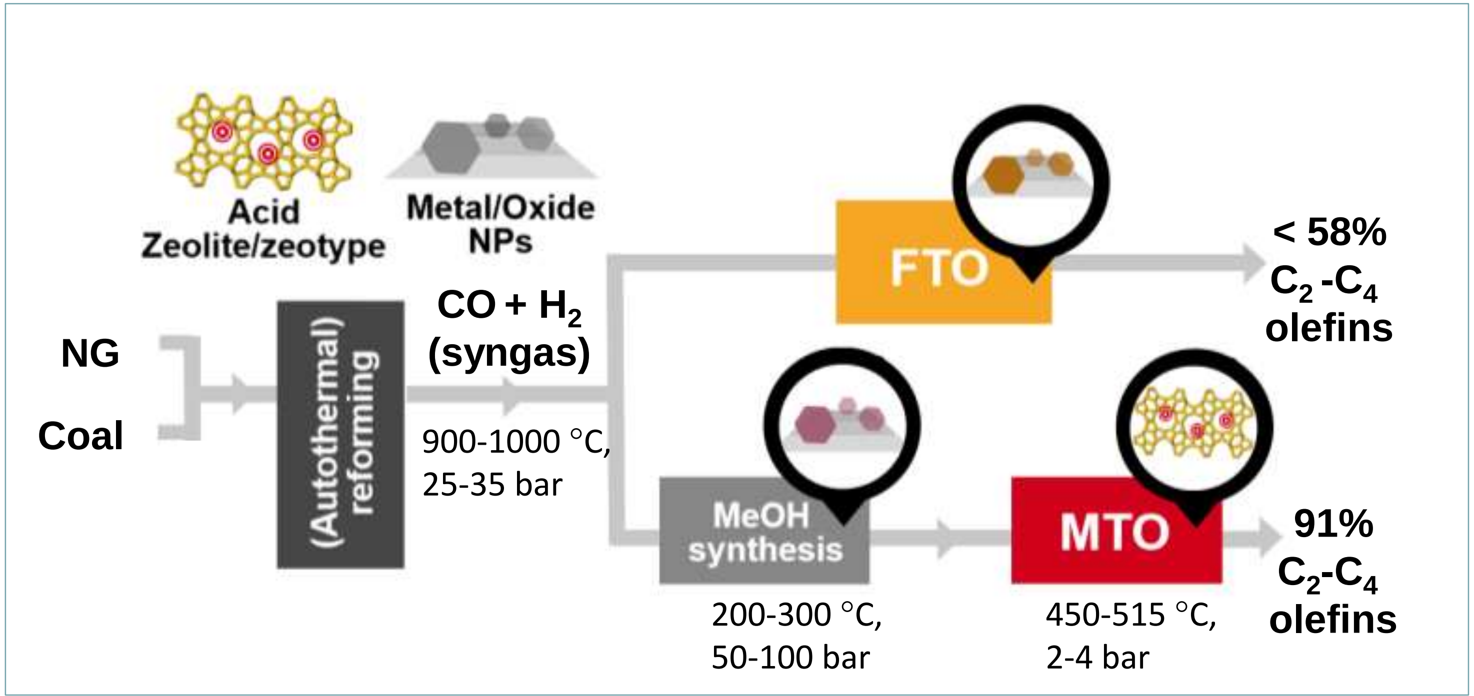
COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.



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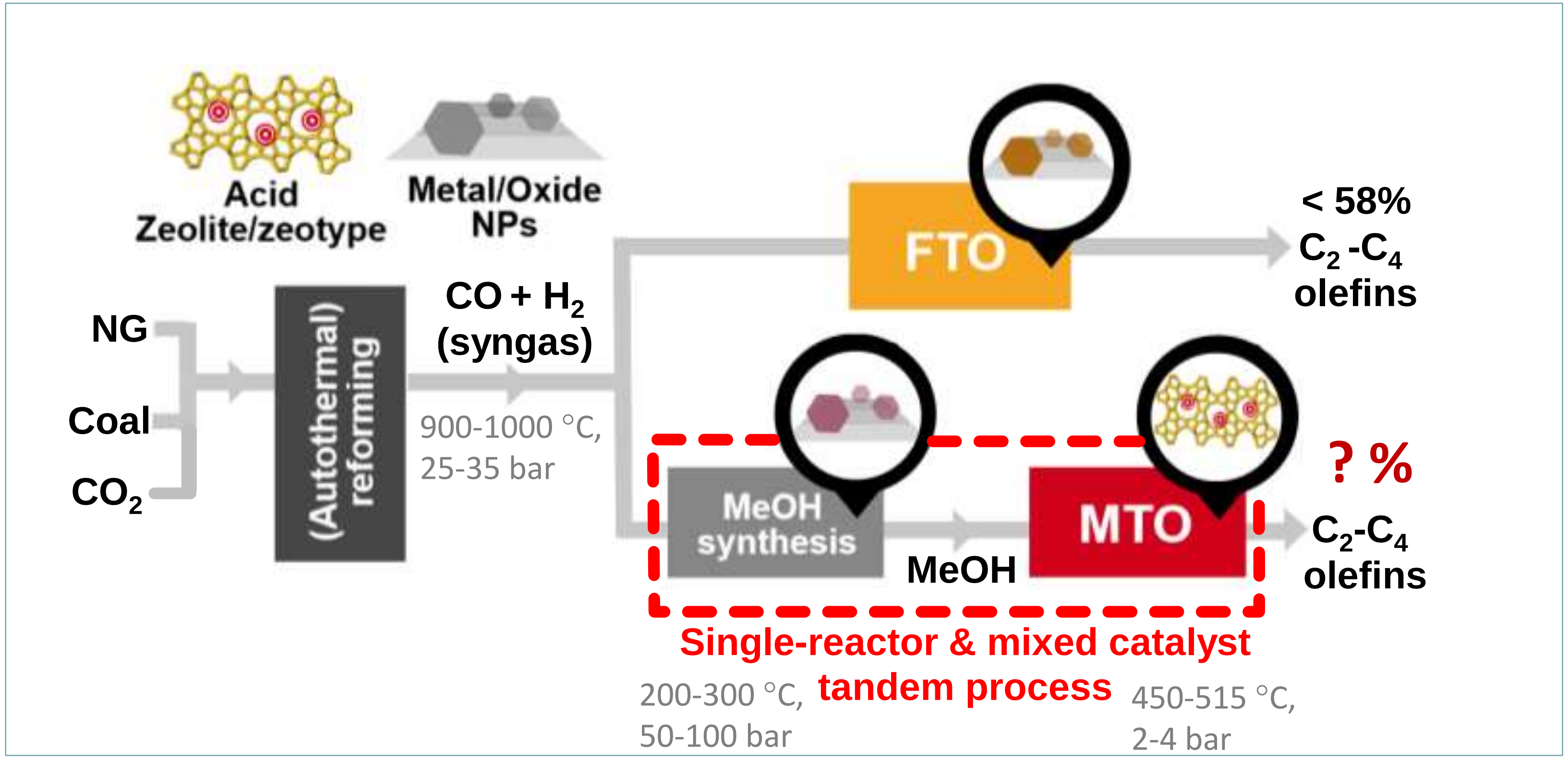

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K. Cheng, Y. Wang et al. *Angew. Chemie Int. Ed.* **2016**, 55, 4725-4728.

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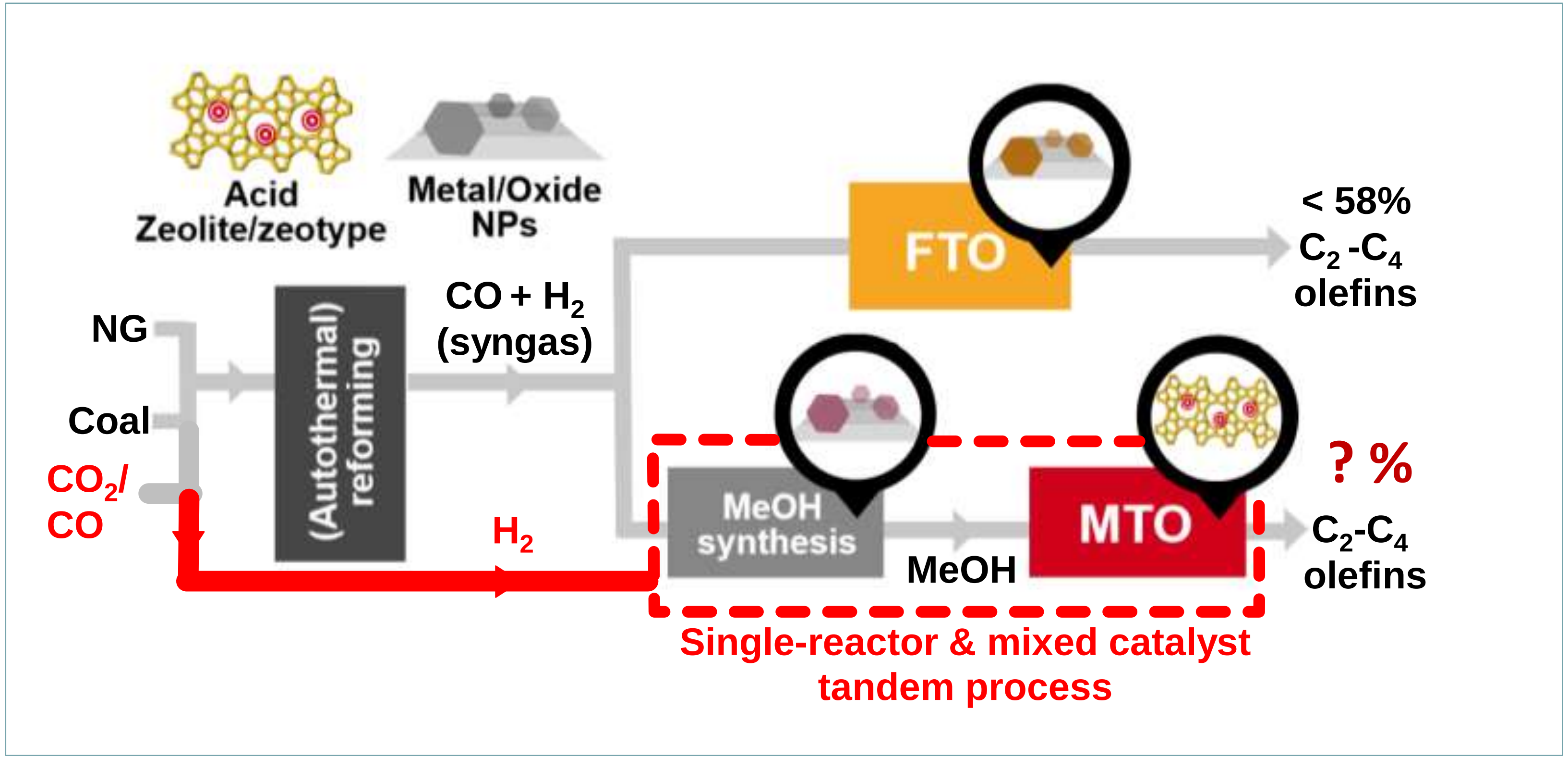

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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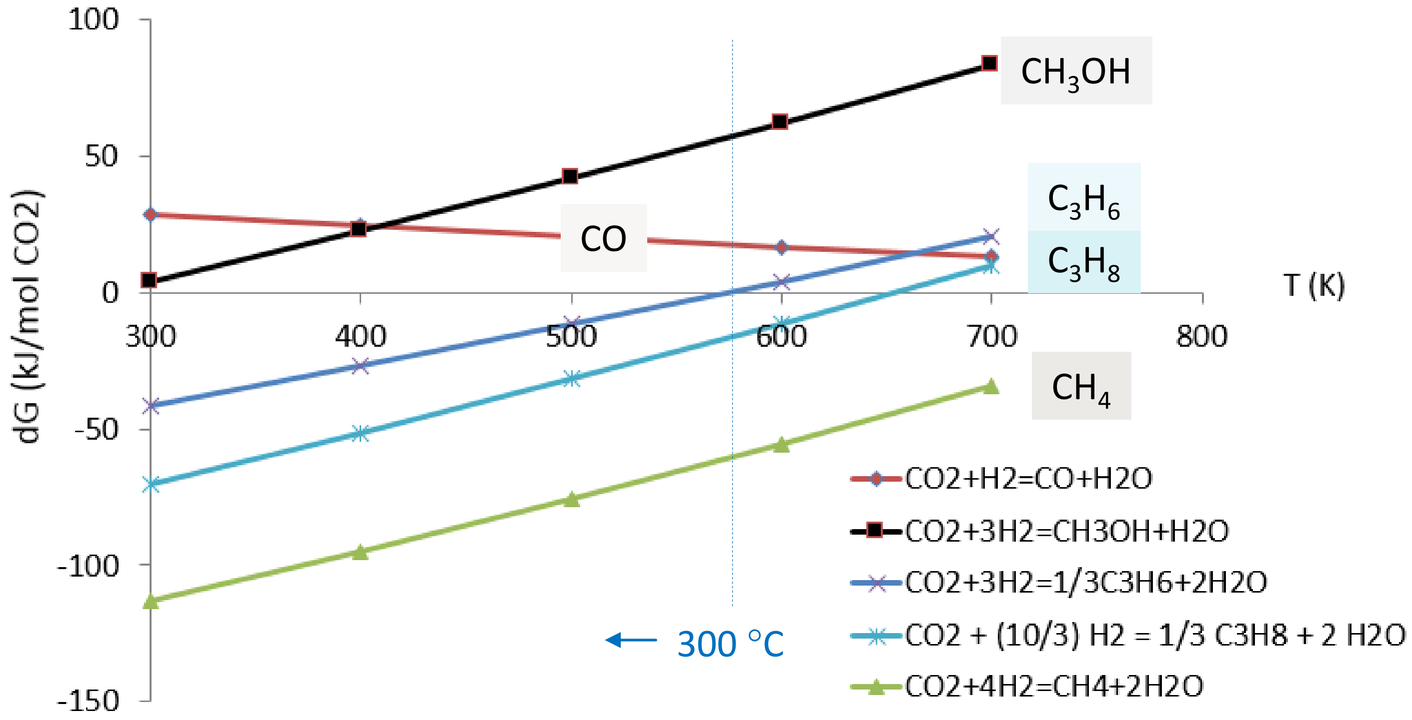
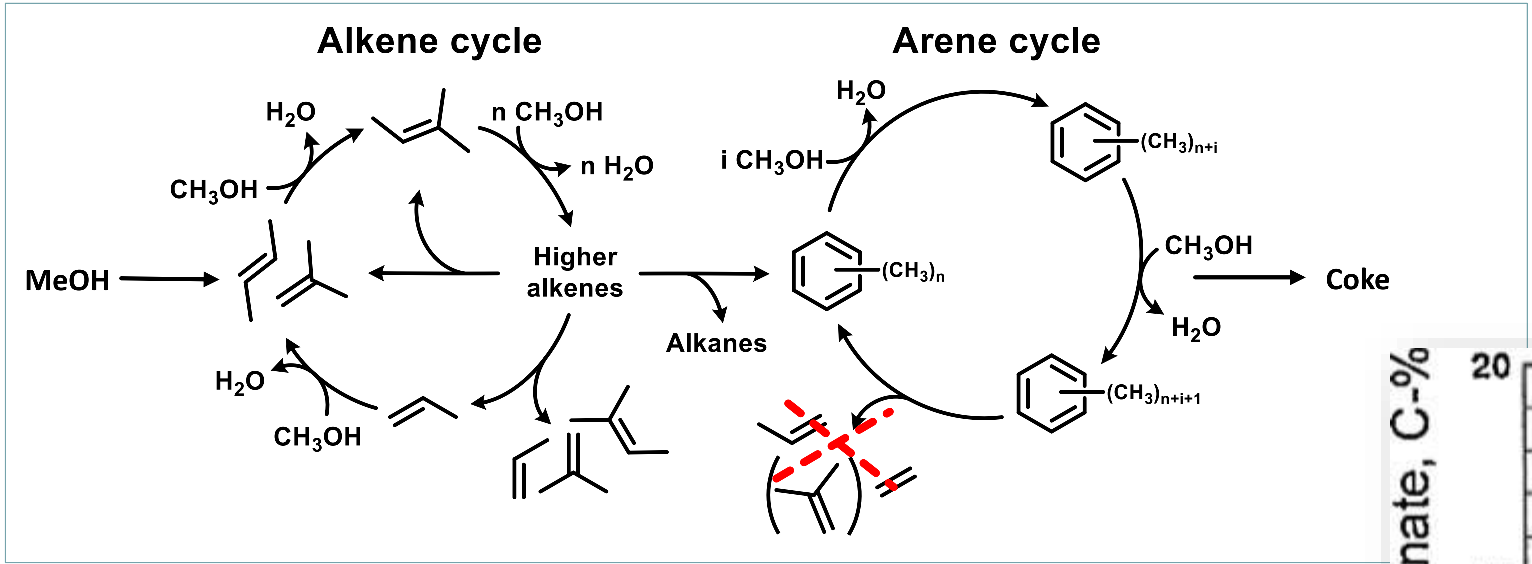
Thermodynamic considerations



Thermodynamic data from TRC Table

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

Tandem catalysis challenges
- The temperature gap -



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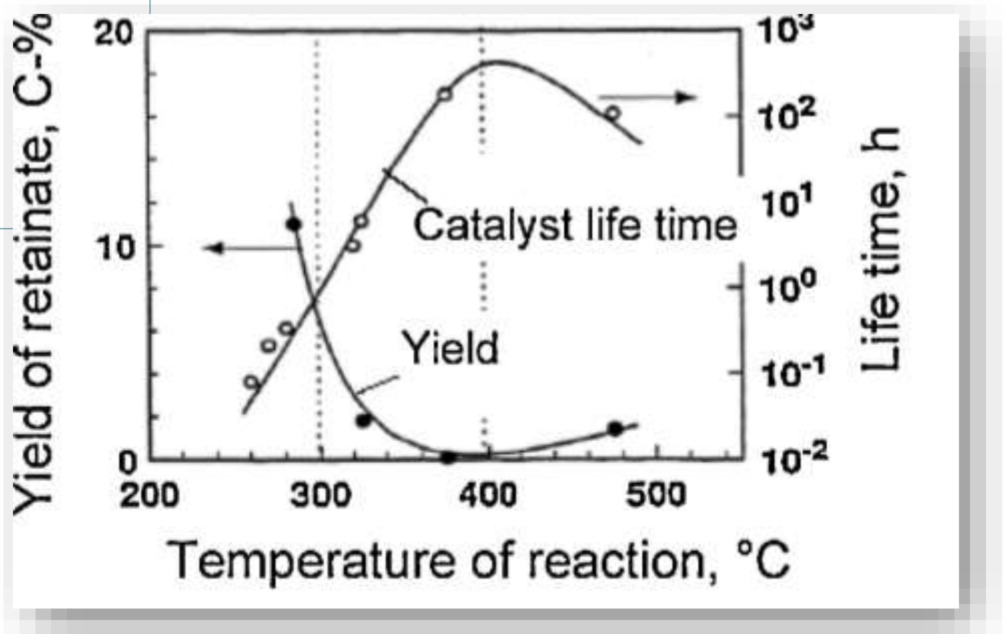

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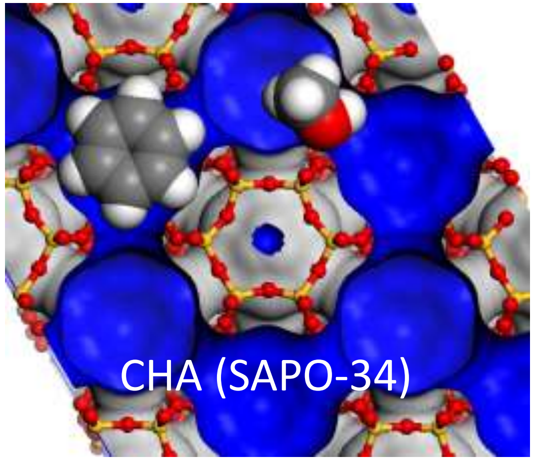
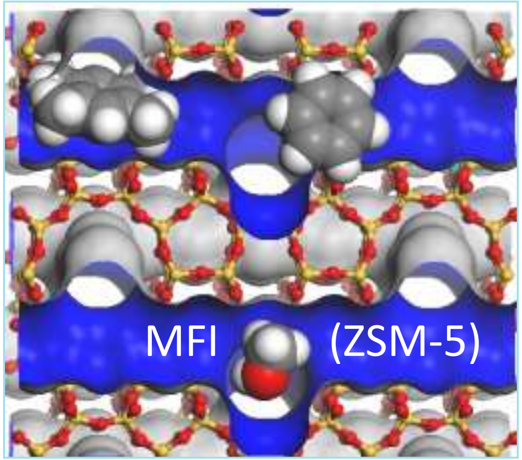
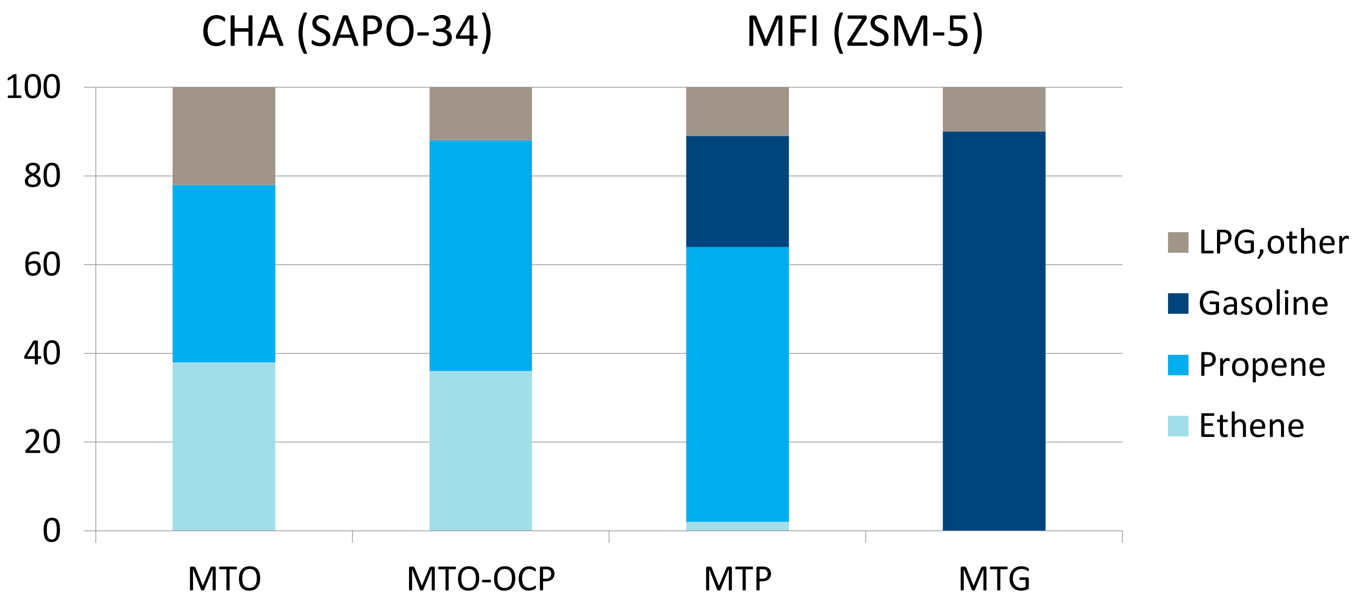
COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

Tandem catalysis: Methanol to propane/propene candidates







460 °C, 1 atm

350 °C, 20 atm

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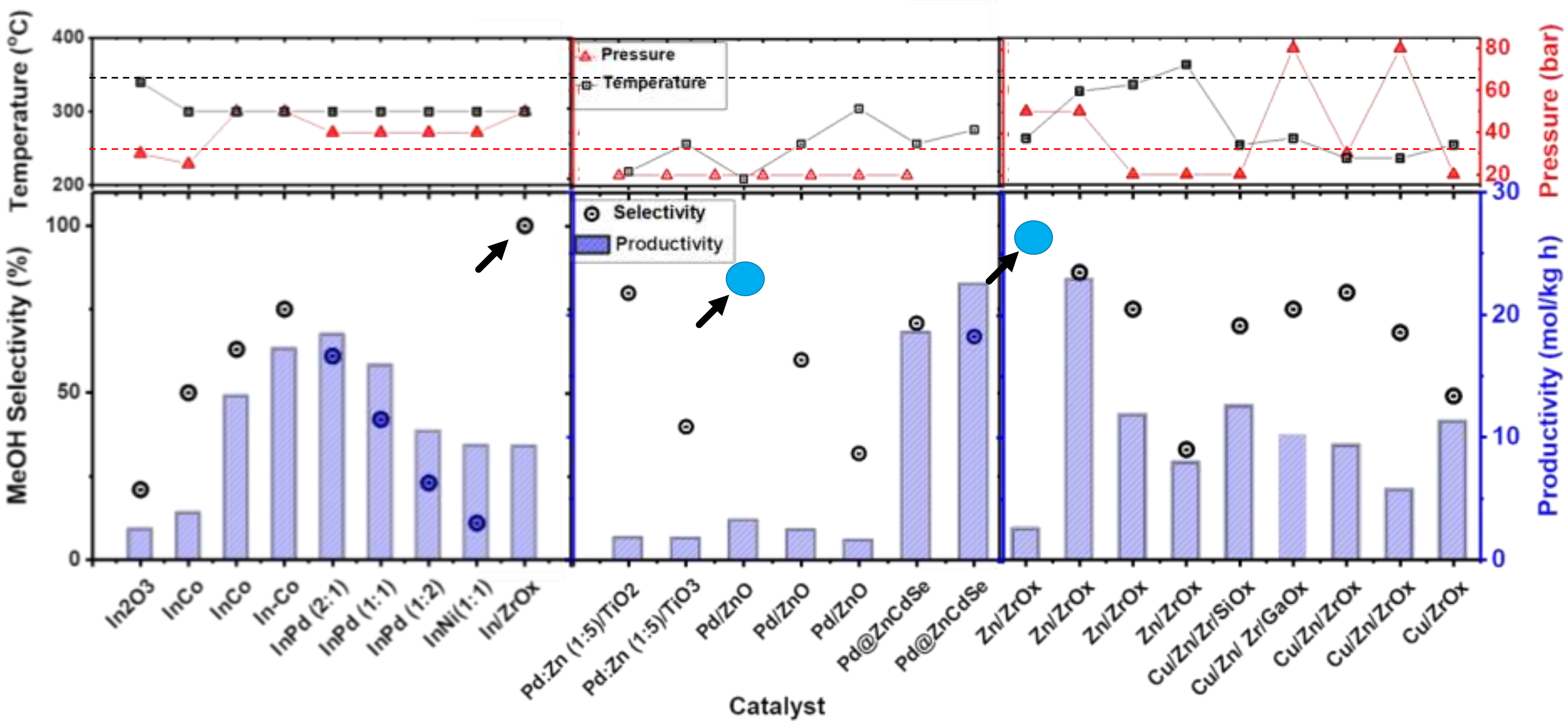
Tandem catalysis: CO_2 hydrogenation candidates



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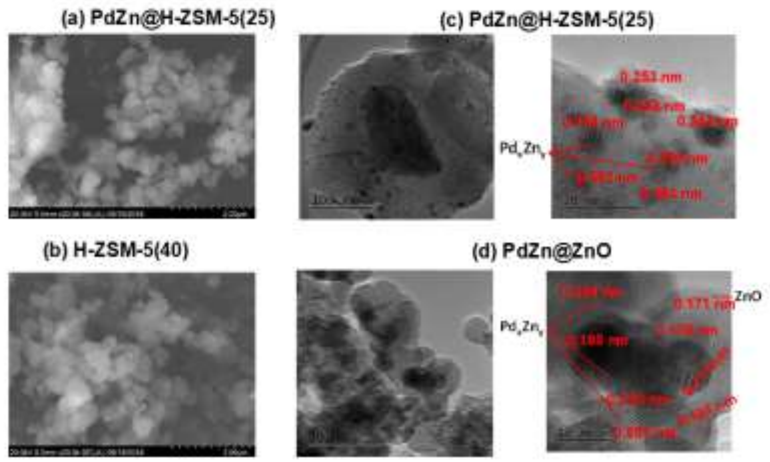
Case 1: PdZn/ZnO + ZSM-5

PdZn@ZnO: Pd salt was impregnated onto ZnO, mixed with H-ZSM-5 and pretreated in H_2 flow at 400 °C for 1 h.

PdZn@H-ZSM-5: Pd complex was grafted onto mesoporous H-ZSM-5, followed by reduction and Zn grafting, and reduction in H_2 at 500 °C for 4 h.

Sample	Elemental composition		Textural properties	
	Si/Al	Zn/Pd	BET area (m^2/g)	Micropore volume (cm^3/g)
H-ZSM-5 (25)	25		420	0.176
PdZn@H-ZSM-5 (25)	25	5	348	0.121
H-ZSM-5 (40)	40		444	0.196
PdZn@ZnO		16		

SEM ***TEM***



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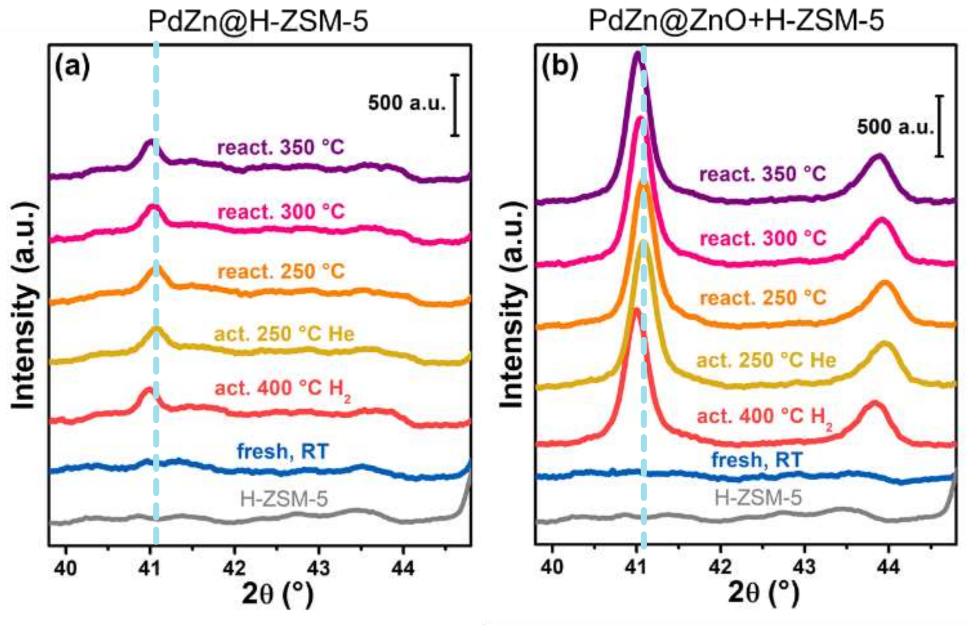
PdZn/ZnO + ZSM5

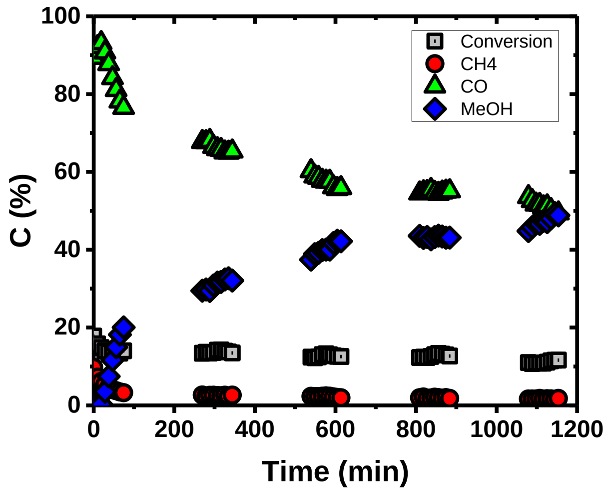
PXRD – PdZn alloy formation



Catalyst testing

300 °C, 20 bar

PdZn@ZnO



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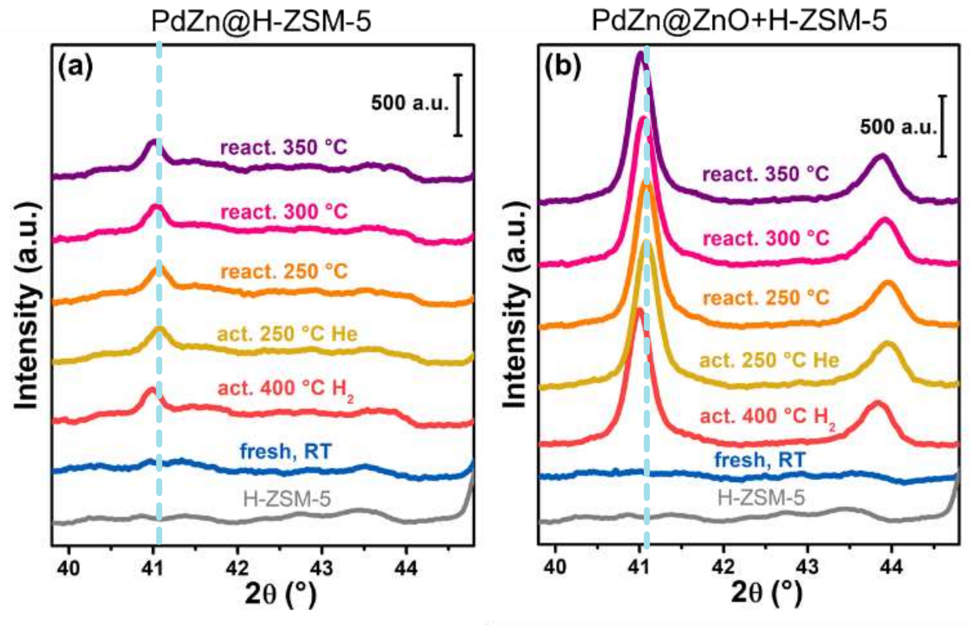
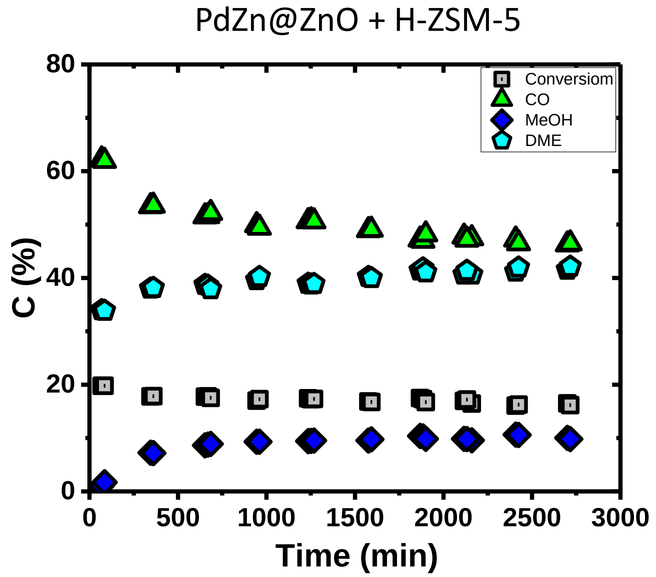
PdZn/ZnO + H-ZSM-5

PXRD – PdZn alloy formation



Catalyst testing

300 °C, 20 bar



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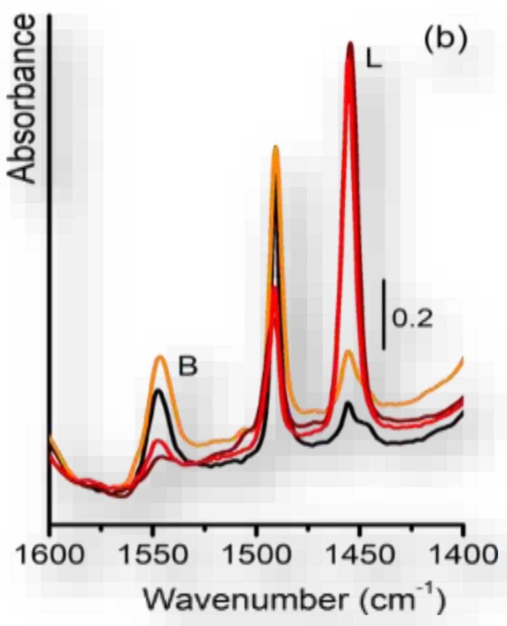
PdZn/ZnO + H-ZSM-5

Acid sites quantification using pyridine FT-IR spectroscopy



Black curve: Parent H-ZSM-5(40),
Orange curve: PdZn@ZnO+H-ZSM-5(40) as-prepared sample,
Red curve: PdZn@ZnO+H-ZSM-5(40) sample treated with H_2 at 400 °C for 1 h,
Brown curve: PdZn@ZnO+H-ZSM-5(40) tested sample.

Sample	Step	Brønsted sites (mmol/g)	Lewis sites (mmol/g)
Fresh H-ZSM-5	Si/Al = 25	0.21	0.07
	Si/Al = 40	0.15	0.07
PdZn@H-ZSM-5 (25)	As prepared	0.02	0.57
	Tested	0.02	0.46
PdZn@ZnO + H-ZSM-5 (40)	As prepared	0.11	0.05
	Activated	0.04	0.25
	Tested	0.03	0.32

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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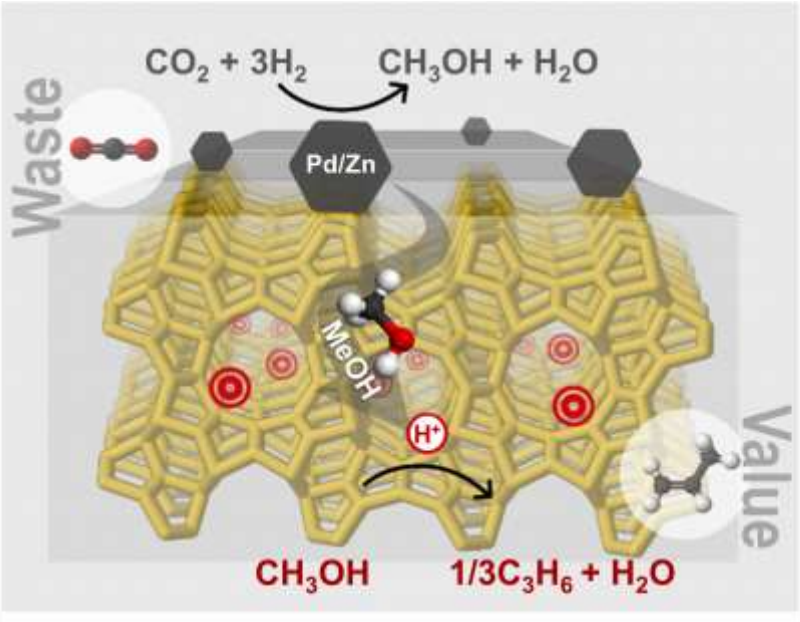
Summary and outlook – Case 1



- **PdZn alloy** maintains high methanol selectivity at 300 °C, and may be suited for the tandem process
- However, excess Zn migrates to the H-ZSM-5 zeolite, where it ion exchanges onto the Brønsted acid sites (confirmed by Zn K edge EXAFS measurements), thereby hindering hydrocarbons formation

***Paper 1*. Ahoba-Sam, C.**; Borfecchia, E.; Lazzarini, A.; Bugaev, A.; Isah, A.A.; Taoufik, M.; Bordiga, S.; Olsbye, U.; **On the conversion of CO_2 to value added products over composite PdZn and H-ZSM-5 catalysts: excess Zn over Pd, a compromise or a penalty?** *Catalysis Science & Technology,* **2020**, *10*, 4373–4385.

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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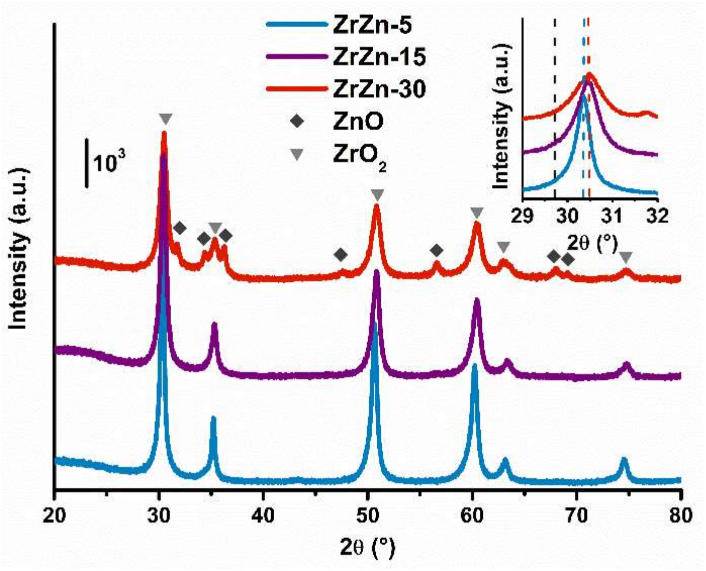
Case 2: $Zr_{1-x}Zn_xO_2$ + H-ZSM-5 (or H-SAPO-34)

$Zr_{1-x}Zn_xO_2$ (X = 0.05, 0.15 or 0.30) was prepared by co-precipitation and eventually mixed with H-ZSM-5 (or SAPO-34) before testing.

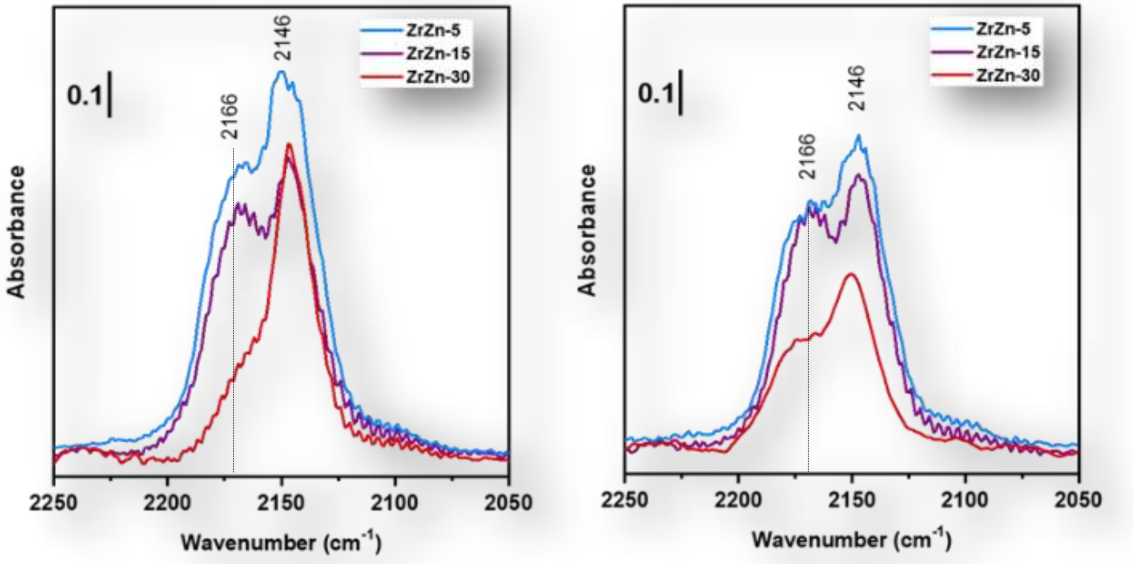
PXRD



FT-IR with CO

Oxidized 400 °C, O_2

Reduced 400 °C, H_2



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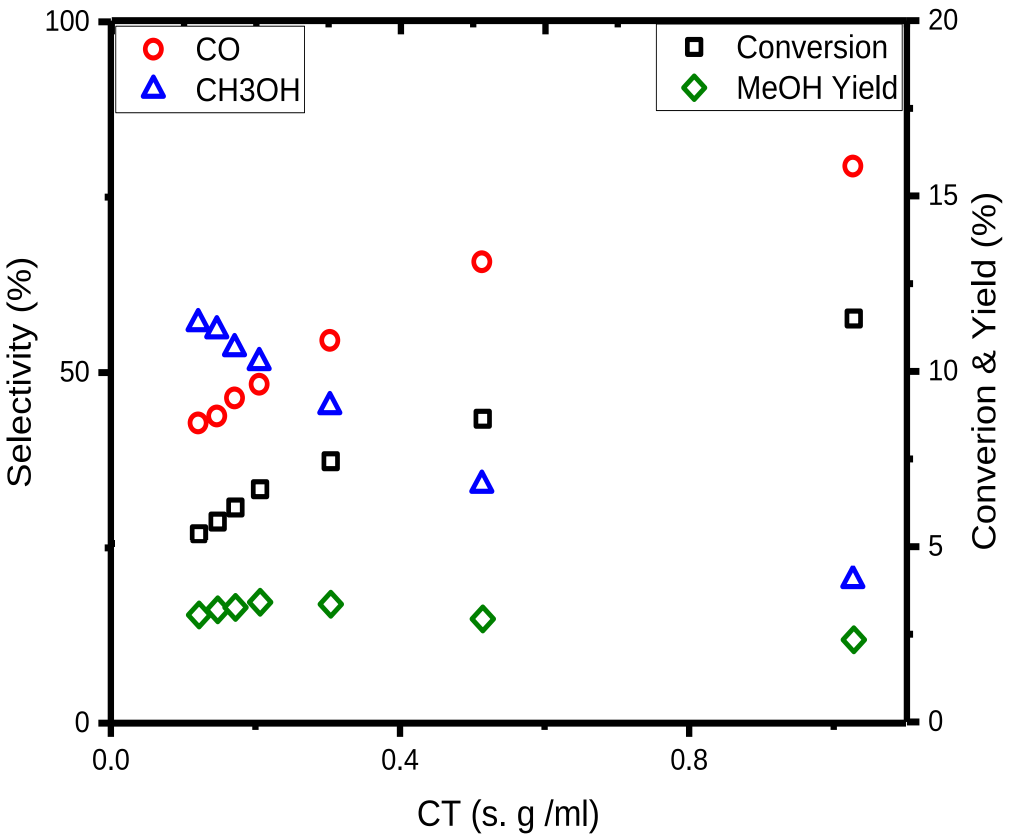
$Zr_{1-x}Zn_xO_2$ alone

Catalytic testing in H_2/CO_2 = 3 at 350 °C, 30 bar



(1) $CO_2 + H_2 \rightarrow CO + H_2O$

(2) $CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O$

(-2) $CH_3OH + H_2O \rightarrow CO_2 + 3\,H_2$

(3) $CH_3OH \rightarrow CO + 2\,H_2$

$$K_{eq,2} = \frac{P(CH3OH)*P(H2O)}{P(CO2)*P(H2)^3}$$

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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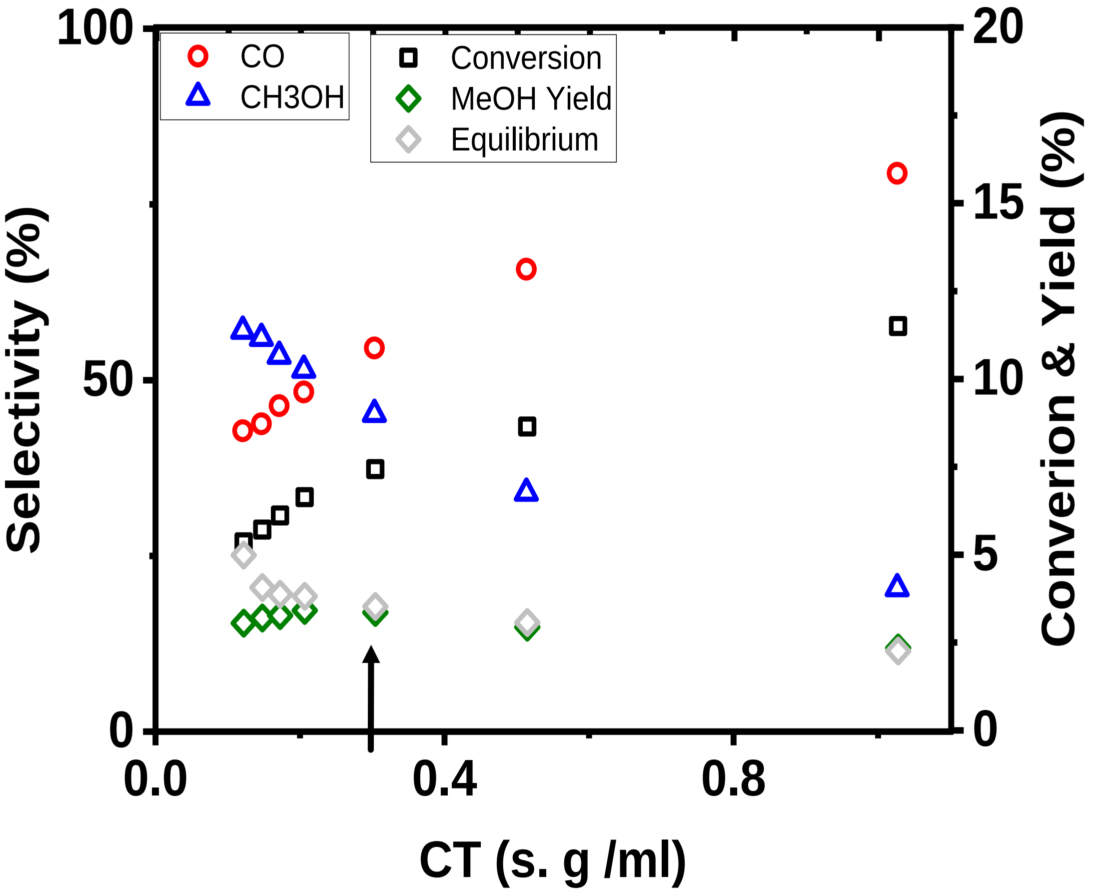
$Zr_{1-x}Zn_xO_2$ alone

Catalytic testing in H_2/CO_2 = 3 at 350 °C, 30 bar



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COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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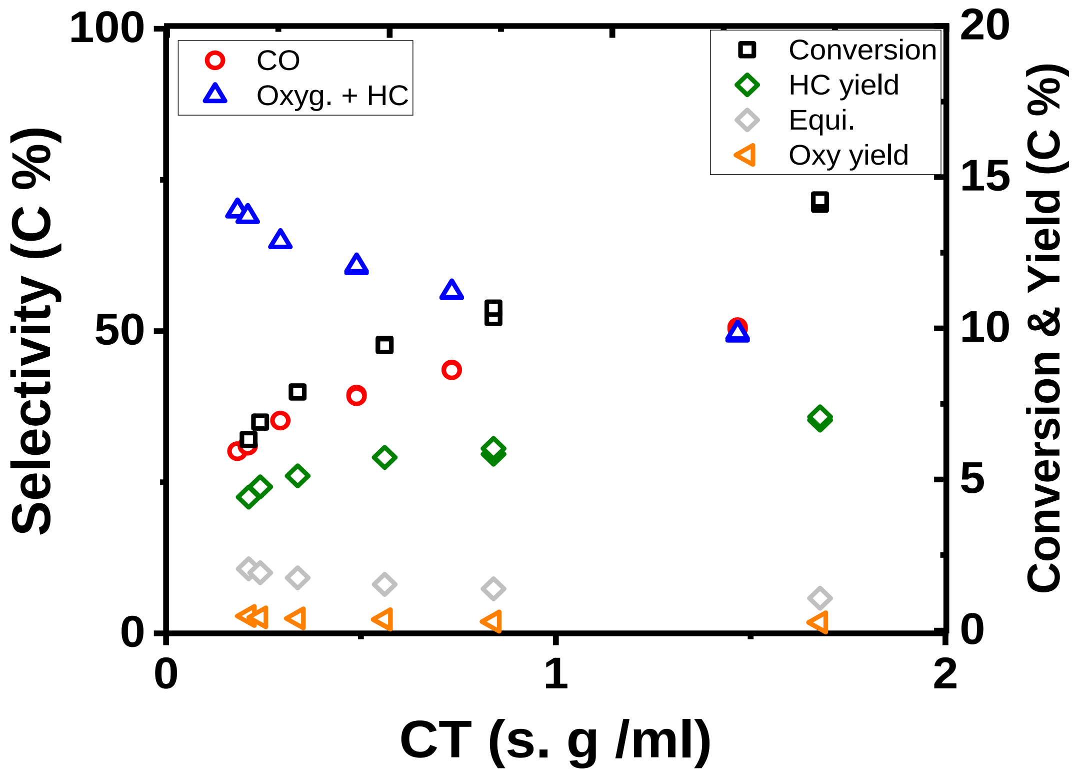
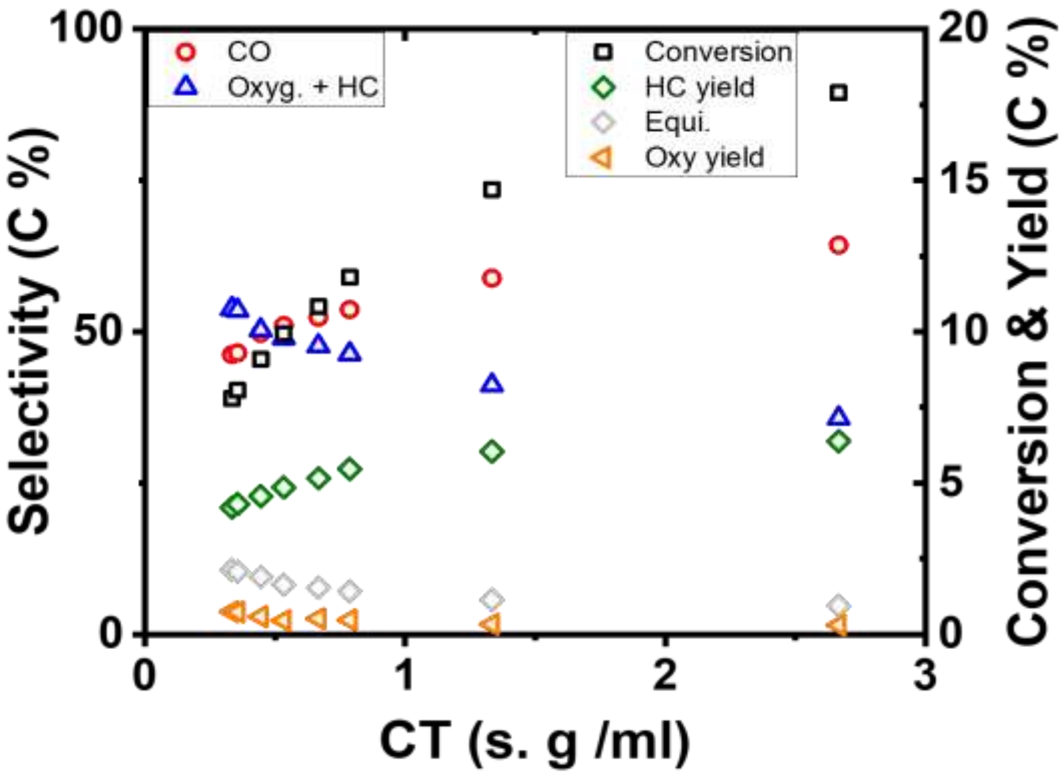
$Zr_{1-x}Zn_xO_2$ + H-ZSM-5

Catalytic testing in H_2/CO_2 = 3 at 350 °C, 30 bar

Si/Al = 25



Si/Al = 360



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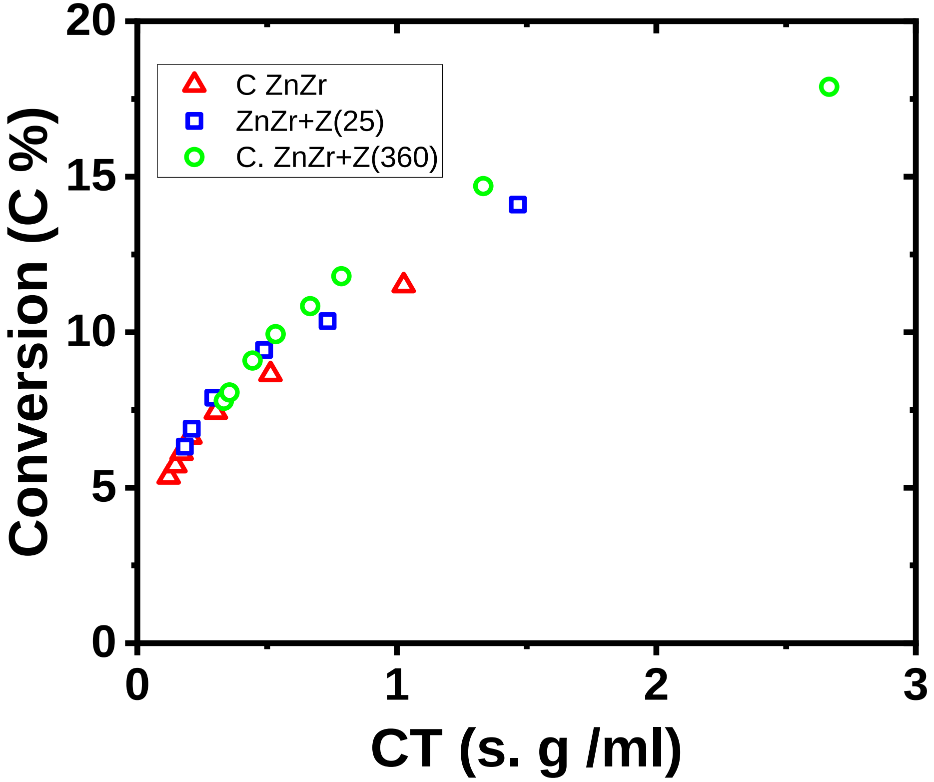
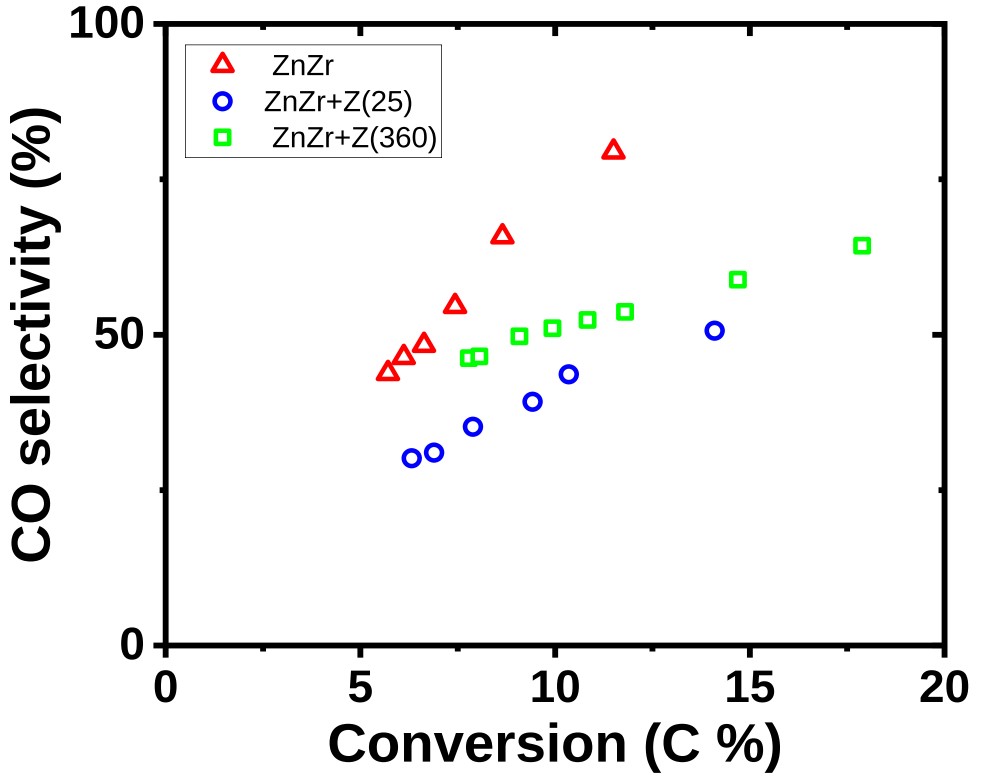
$Zr_{1-x}Zn_xO_2$ + H-ZSM-5

Catalytic testing in H_2/CO_2 = 3 at 350 °C, 30 bar

CO_2 conversion



CO selectivity



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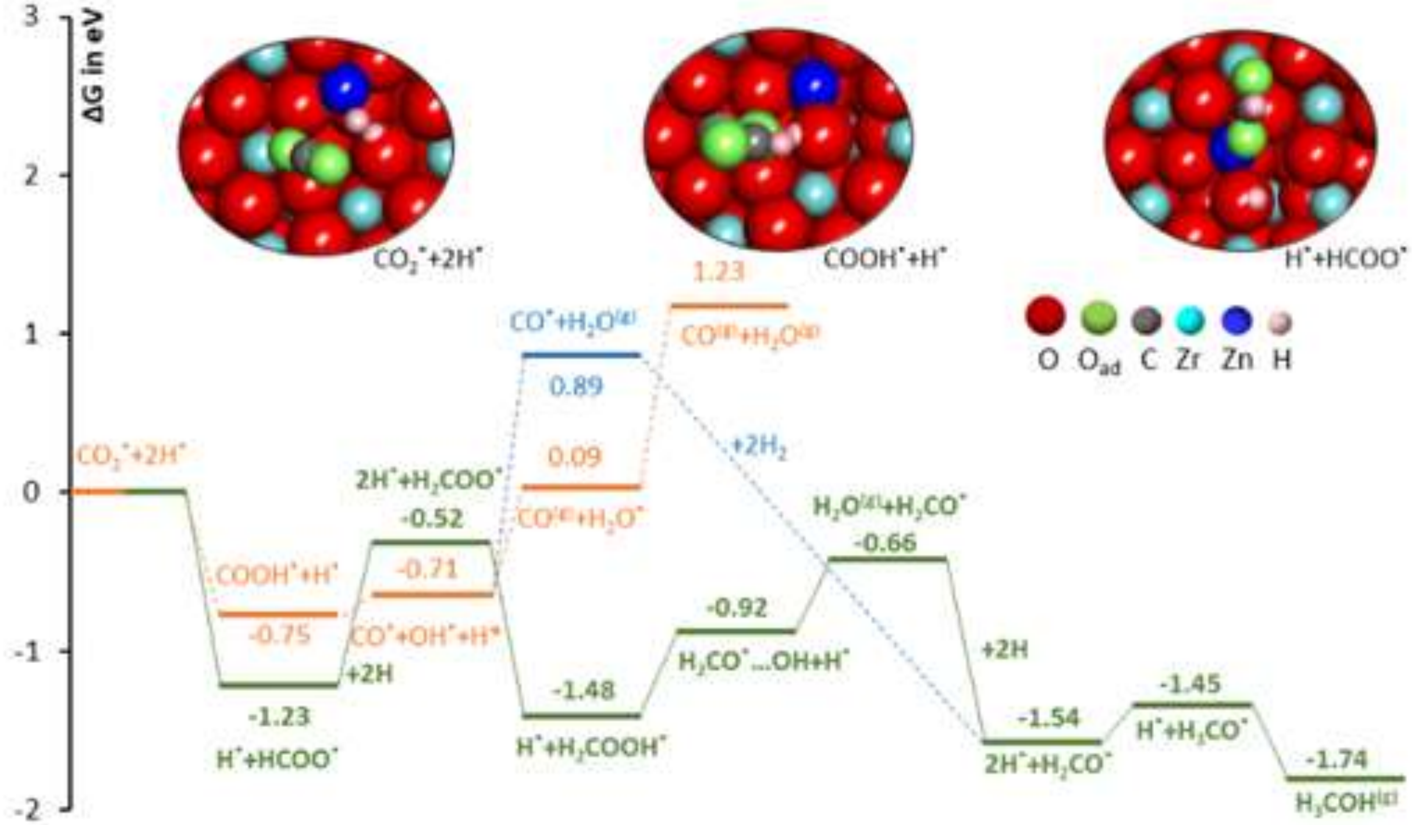
ZnZrO – computational studies



COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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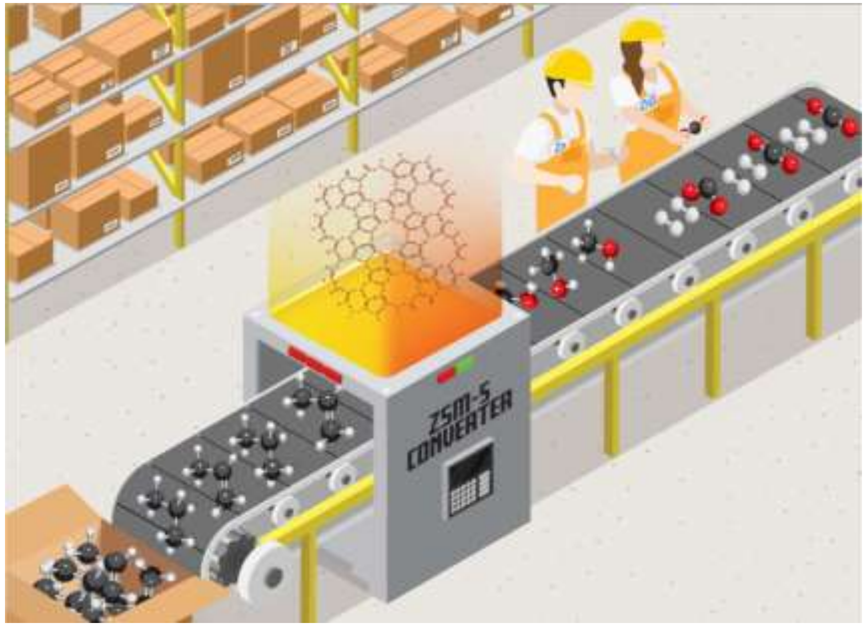
Summary and outlook – Case 2



- Studies of the **ZnZrO+H-ZSM-5** system shows that methanol is a primary product from CO_2, and both CO and hydrocarbons are formed from methanol, over the tandem catalyst
- Methanol is formed via the formate route over ZnZrO
- CO_2 hydrogenation is the rate-limiting step of the tandem reaction

***Paper 2*. Ticali, P**.; Salusso, D.; Ahmad, R.; Ahoba-Sam, C.; Ramirez, A.; Shterk, G.; Lomachenko, K.A.; Borfecchia, E.; Morandi, S.; Cavallo, L.; Gascon, J.; Bordiga, S.; Olsbye, U. **CO_2 hydrogenation to methanol and hydrocarbons over bifunctional Zn-doped ZrO_2/Zeolite catalysts**. *Catalysis Science & Technology,* **2020**, *https://doi.org/10.1039/D0CY01550D*.

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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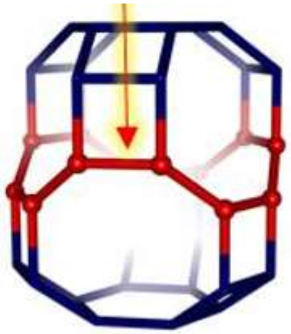
Case 3: ZnCeZrO + H-RUB-13

SAPO-34



RUB-13

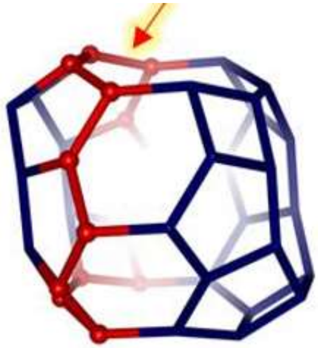
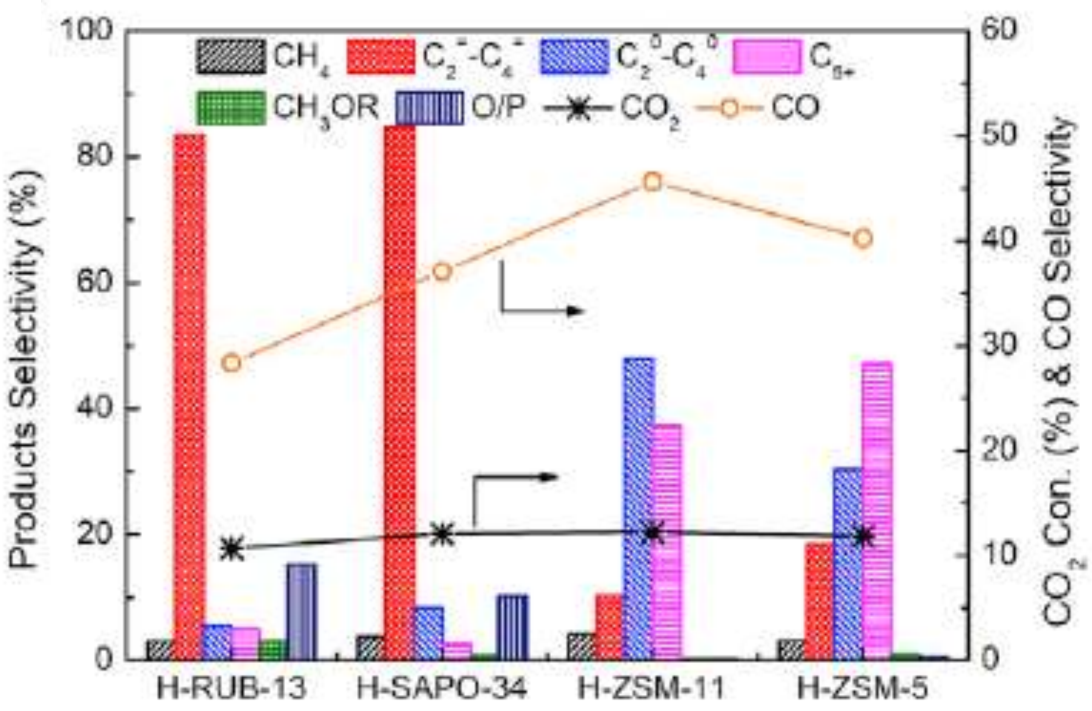


Illustration from: J. H. Kang, J.H et al., *ACS Catal.* **2019**, 9, 6012.



$Zn_{0.5}Ce_{0.2}Zr_{1.8}O_4$ + zeolite, 350 °C, 10 bar, H_2/CO_2 = 3:1, GHSV = 4,800 mL/gh

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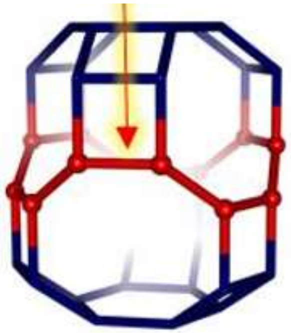
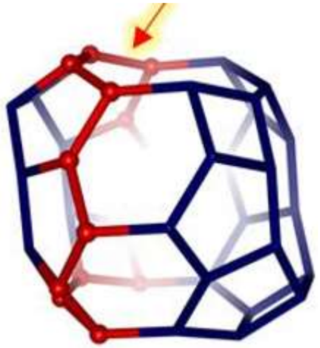
ZnCeZrO + H-RUB-13

SAPO-34



RUB-13



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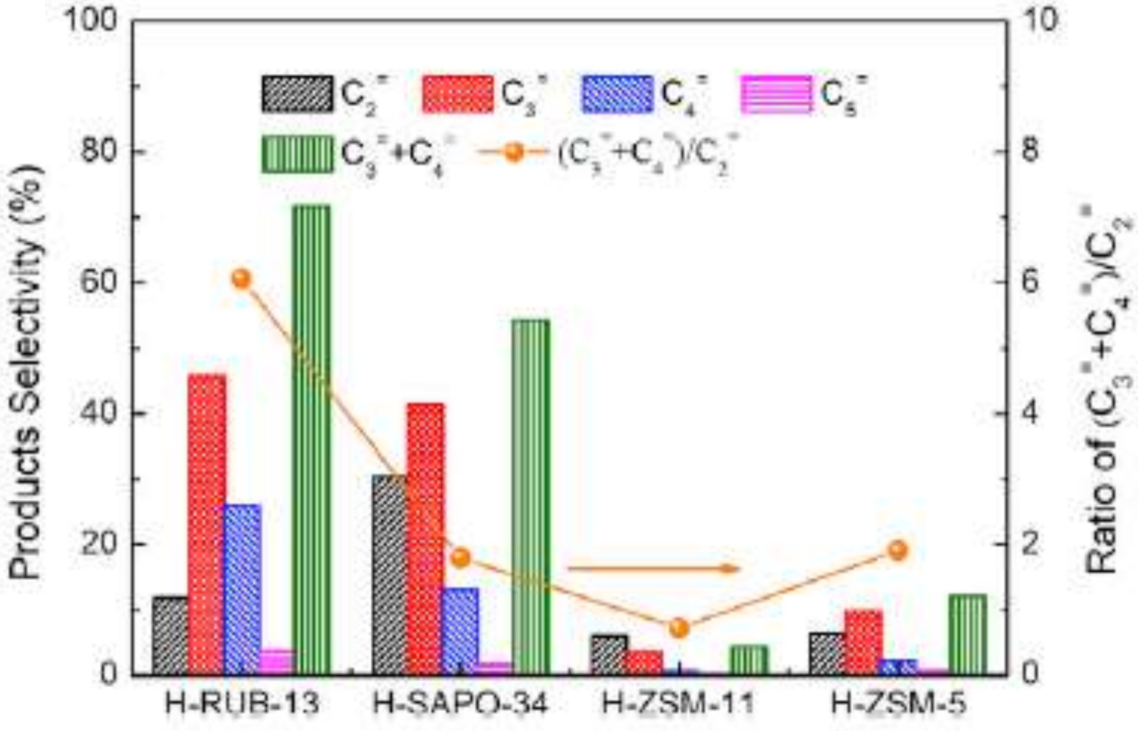

$Zn_{0.5}Ce_{0.2}Zr_{1.8}O_4$ + zeolite, 350 °C, 10 bar, H_2/CO_2 = 3:1, GHSV = 4,800 mL/gh

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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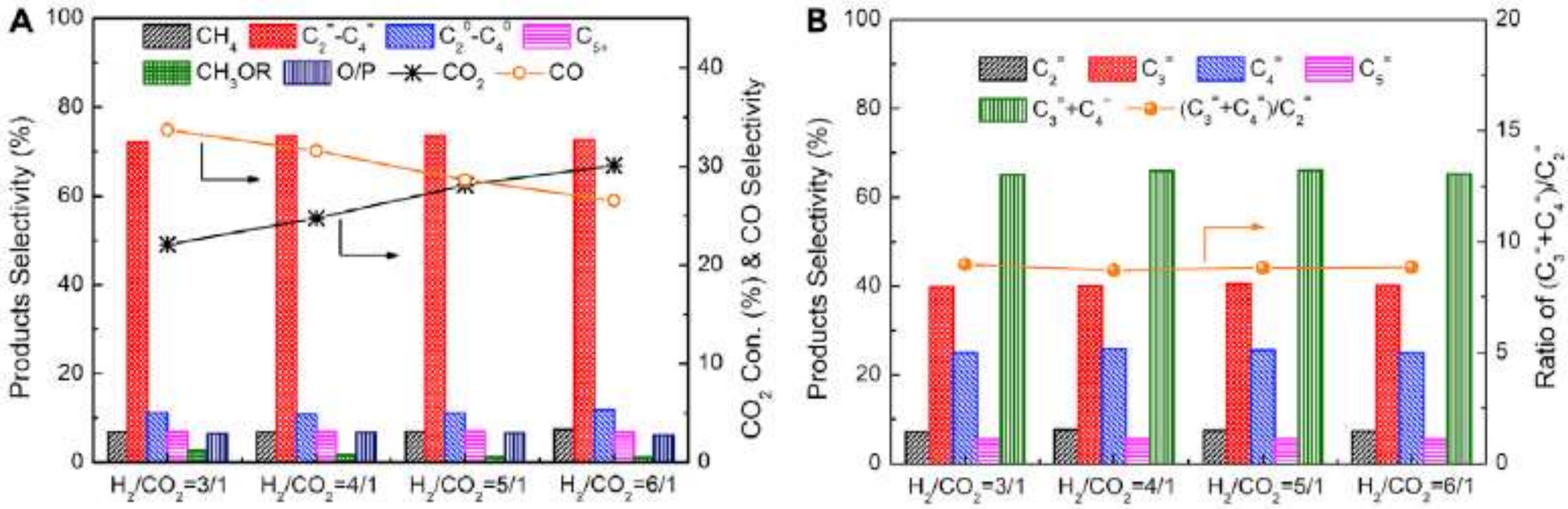
CO2MOS

ZnCeZrO + H-RUB-13

Influence of test conditions



$Zn_{0.5}Ce_{0.2}Zr_{1.8}O_4$: RUB-13 = 1:2, 350 °C, 35 bar, H_2/CO_2 = 3:1 – 6:1

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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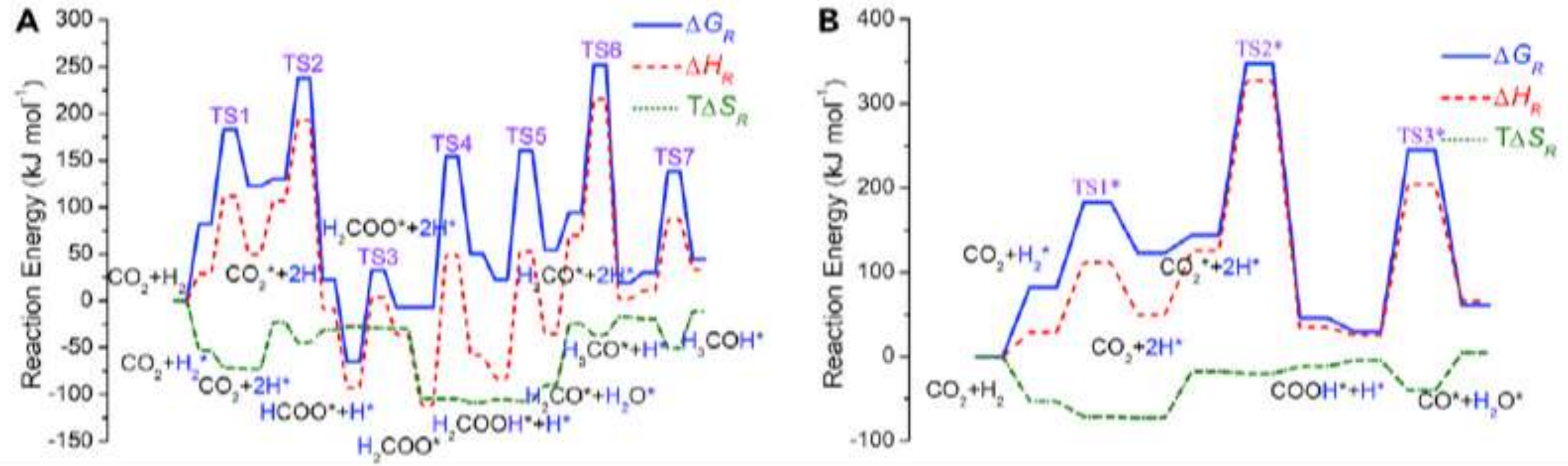
ZnCeZrO + RUB-13



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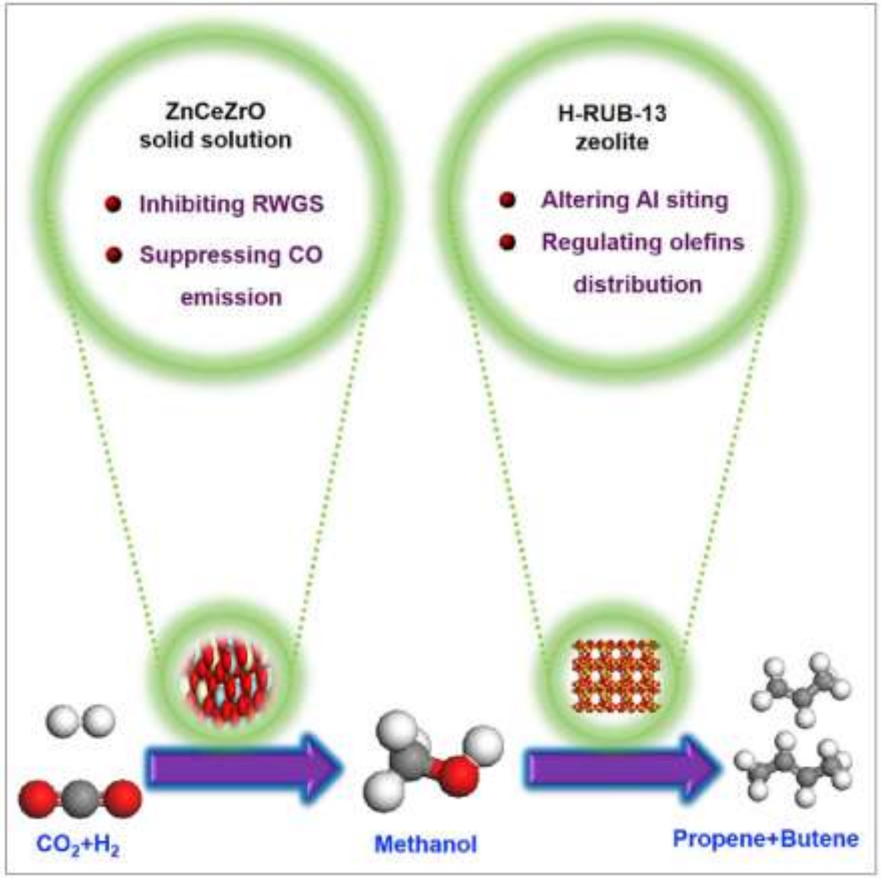
Summary and outlook – Case 3



- Studies of the **ZnCeZrO+H-RUB-13** system shows that small changes in the cavity-window size of the zeotype has substantial impact on hydrocarbon product distribution.

- $C_3^=$ and $C_4^=$ account for 90% of light olefins due to the promotion of the alkene-based cycle

- CH_3OH is formed on $Zn_{0.5}Ce_{0.2}Zr_{1.8}O_4$ via the formate - methoxyl intermediates mechanism.

***Paper 3*. Wang, S**.; Zhang, L.; Zhang, W.; Wang, P.; Qin, Z.; Yan, W.; Dong, M.; Li, J.; Wang, J.; Lin He,L.; Olsbye, U.; Fan, W., **Selective conversion of CO_2 into Propene and Butene**. *Chem* **2020**, *6, 1-20.*

This project has received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

Conclusions and Outlook

Case 1. Studies of the **PdZn+H-ZSM-5** system shows that methanol selectivity of PdZn/ZnO may be maintained under MTO-relevant conditions, but leaching of Zn into the zeolite, thereby poisoning the Brønsted acid sites, is a challenge.

Case 2. Studies of the **ZnZrO+H-ZSM-5** system shows that methanol is a primary product from CO_2, and both CO and hydrocarbons are formed from methanol, over the tandem catalyst. CO_2 hydrogenation is the rate-limiting step of the tandem reaction.

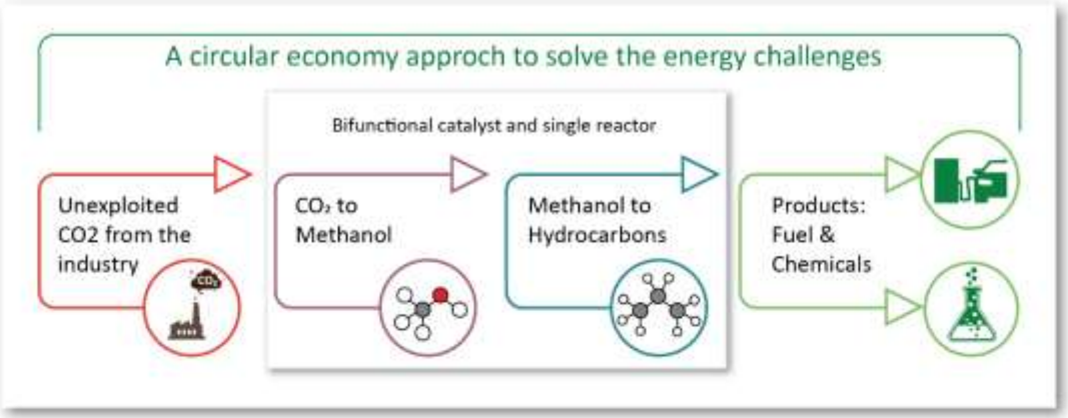
Case 3. Studies of the **ZnCeZrO+H-RUB-13** system shows that small changes in the cavity-window size of the zeotype has substantial impact on hydrocarbon product distribution. CH_3OH is formed selectively on $Zn_{0.5}Ce_{0.2}Zr_{1.8}O_4$ via the formate - methoxyl intermediates mechanism

Overall, the three case studies yield important insight in function – performance correlations for the methanol-mediated conversion of CO_2 and H_2 to propane and propene

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
This project has received funding from the European Union’s Horizon 2020 research and innovation programme under Grant Agreement No. 837733.

CO2MOS

Efficient CO_2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS



Thanks to all COZMOS WP1 partners for their contributions, and

Thank you for your attention!

COZMOS: Efficient CO2 conversion over multisite Zeolite-Metal nanocatalysts to fuels and OlefinS.
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INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILIZATION
TU/E - EINDHOVEN - 16-17 FEBRUARY 2021

CO_2 Capture Using 3D Printed PEI Adsorbents Supported By Carbon Nanostructures

Shreenath Krishnamurthy[1], Richard Blom[1], Carlos Adolfo Grande[1], Kari Anne Andreassen[1], Vesna Middelkoop[2], Marleen Rombouts[2] and Adolfo Bendito Borras[3]

1. SINTEF Industry, Oslo, Norway 2. VITO, Mol, Belgium 3. AIMPLAS, Valencia, Spain

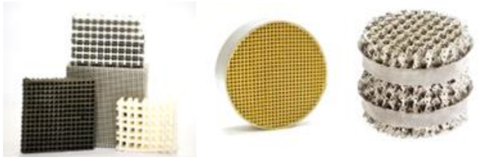
Shreenath.Krishnamurthy@sintef.no

CARMOF

SINTEF 70 years 1950-2020 vito AIMPLAS PLASTICS TECHNOLOGY CENTRE

Introduction

High pressure drop



Low pressure drop and better mass transfer

- CO_2 capture from power plants is associated with large capture footprint
- Fast cycling and higher flowrates can lower footprint
- Structured sorbents are advantageous over pellets for lowering the footprint
- 3D printing offers good control over shape of the sorbent and channel geometry
- Aim of this work : Evaluate a 3D printed monolith for post-combustion carbon capture: From equilibrium data to process simulations

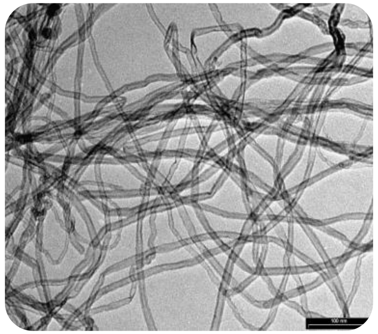
3D printing by Micro-Extrusion / Robocasting

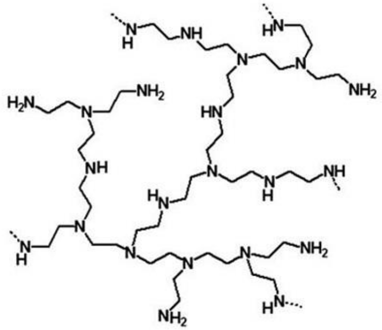
PEI-CNT-water based viscous paste

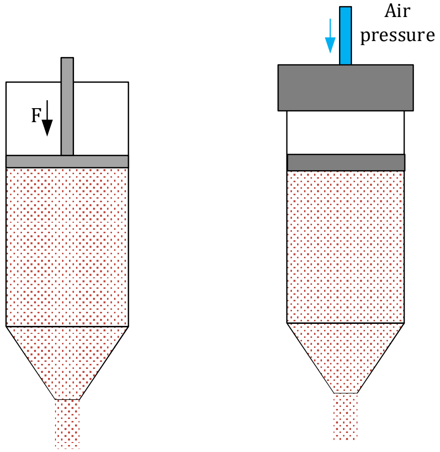
Extrusion through nozzle **at room temperature**

Computer controlled deposition of fibres

Drying

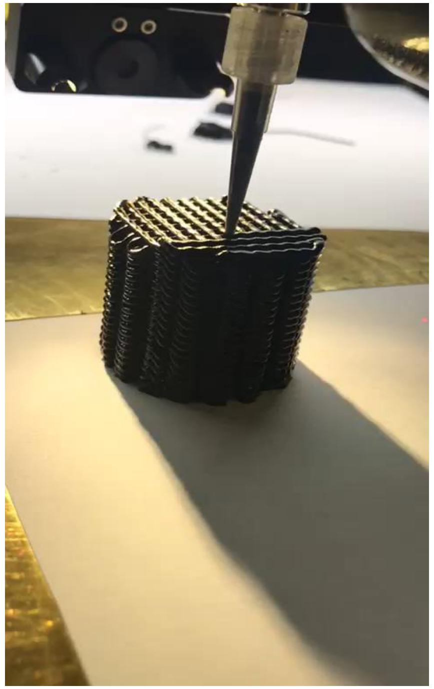


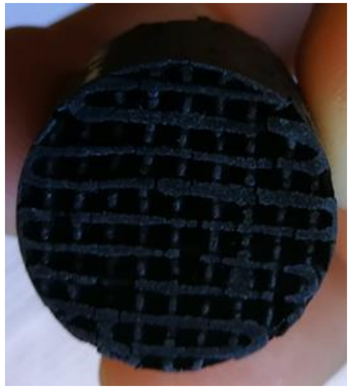




Nozzle diameter 1.2mm

Piston-based and pneumatic dispensing

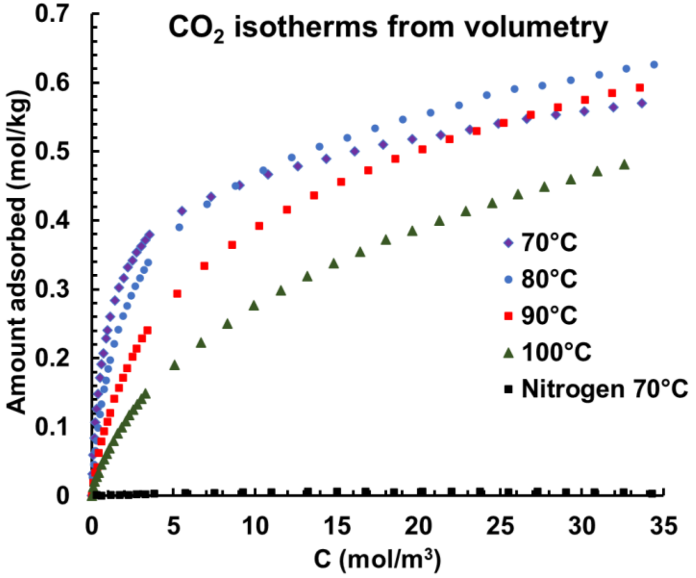


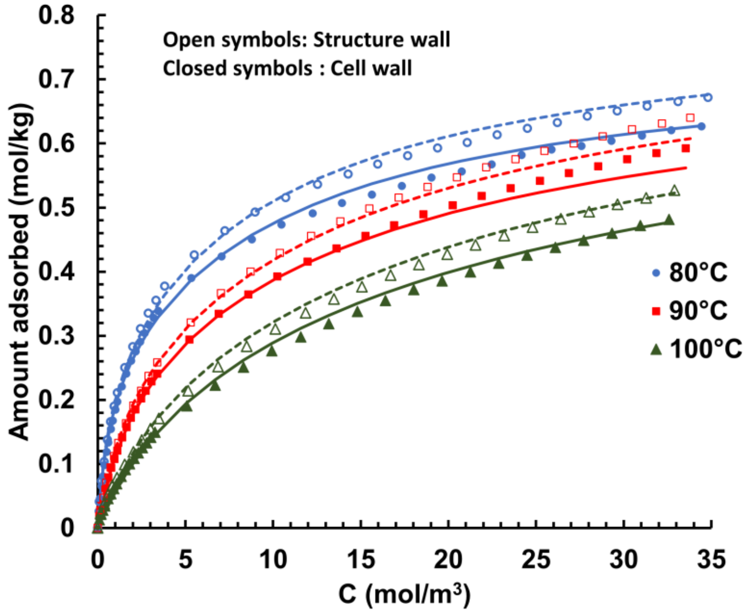


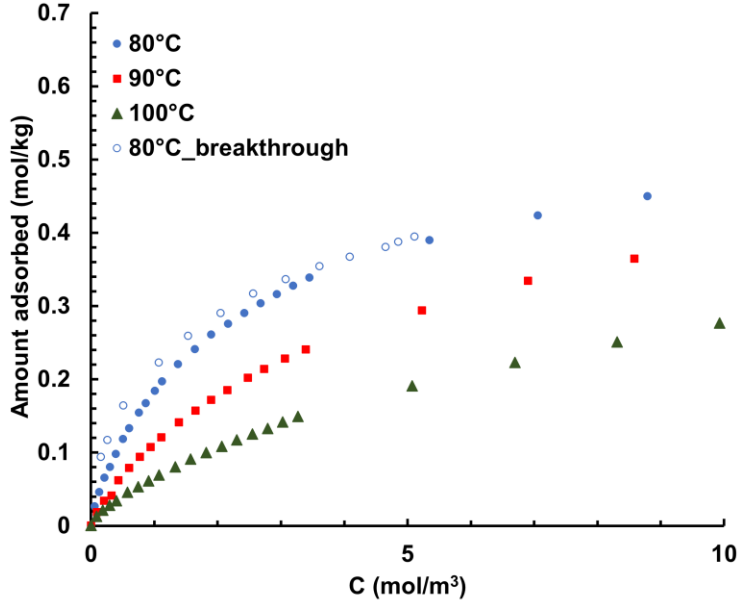
Furnace drying at 40°C

Channel diameter 1.4 mm
Wall thickness 0.6 mm

CO_2 adsorption equilibrium







- Volumetric experiments to measure adsorption isotherms
- One structure was crushed and isotherms on cell wall material and monolith wall material measured for different temperatures
- Breakthrough experiments carried out with 15% CO_2 in N_2 feed, desorption with pure N_2
- Heat of adsorption for CO_2 = –100 kJ/mol, CO_2 adsorption capacity at 0.15 bar and 90°C = 0.3 mol/kg
- Minor variations observed in CO_2 adsorption capacity within the 3D printed adsorbent

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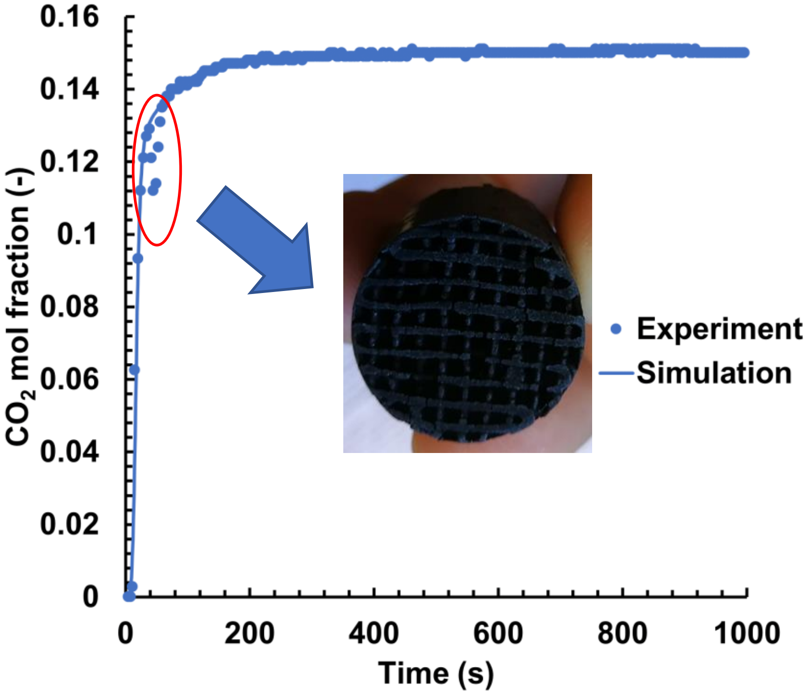
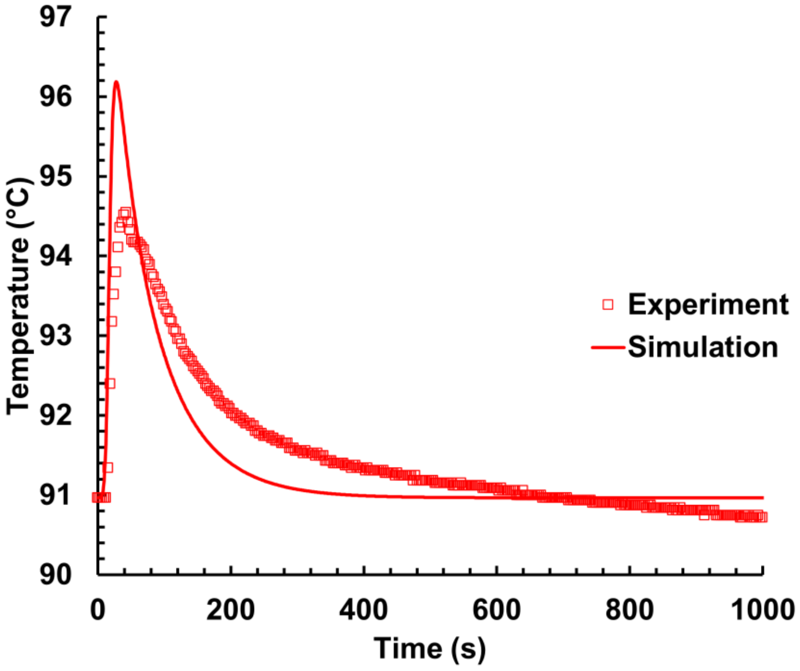
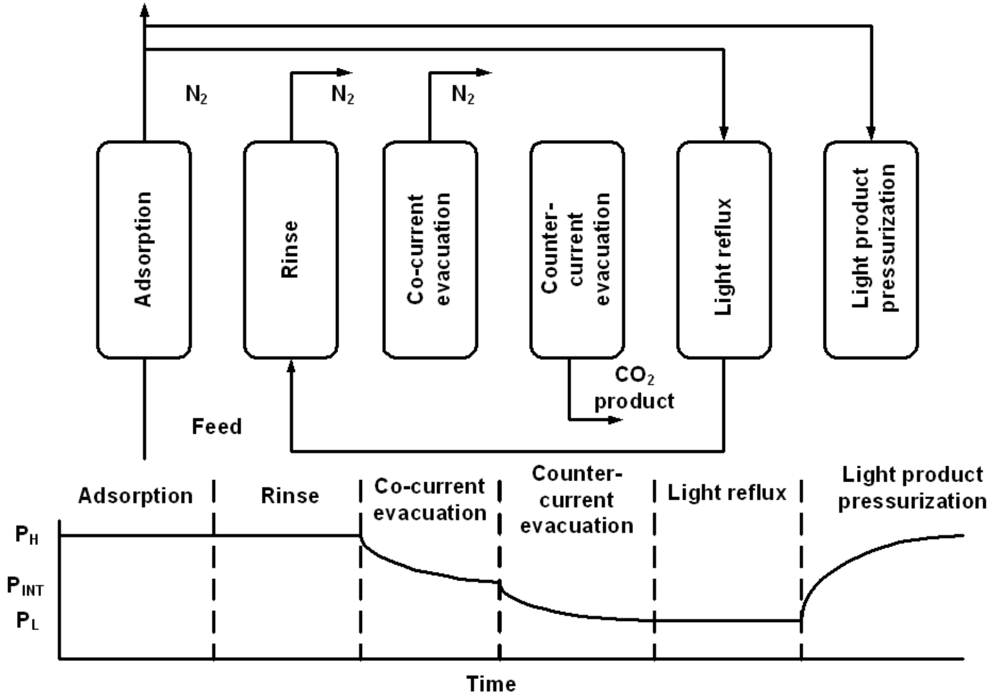
CO_2 adsorption kinetics





- Dynamic column breakthrough experiments (2 structures stacked one on top of the other, 15% CO_2, 85% N_2)
- Adsorption part of the breaktrhough experiments analysed with a 1D process model
- Fitting the LDF and heat transfer co-efficient values for 3 temperatures.

Process simulation and optimization



6-step VSA cycle[3]

The system : 15% CO_2 , 85% N_2 , 90°C
Length of column 1 m : diameter 0.29 m
Isotherms and LDF coefficient values obtained from volumetry and breakthrough
1D non-isothermal, non-isobaric model

Pressure drop[1]

$$\frac{-dP}{dZ} = \frac{28.4u\mu}{d_{ch}^2}$$

Axial dispersion[2]

$$D_L = D_m + \frac{(2ud_{ch})^2}{192D_m}$$

$$\mathbf{CO_2\ purity} = \frac{\textbf{mass CO2 in evac}}{\textbf{total mass evac}}$$

$$\mathbf{Productivity} = \frac{\textbf{mass CO}_2\textbf{ in } \textit{evacuation}}{\textbf{volume of adsorbent X cycle time}}$$

$$\mathbf{CO_2\ recovery} = \frac{\textbf{mass CO2 in evac}}{\textbf{mass CO2 in feed}}$$

$$\textbf{Specific energy} = \frac{\textbf{Compression+Evacuation energy}}{\textbf{mass CO2 in evacuation}}$$

Aim of process study

- Identify minimum specific energy and maximum productivity
- Target CO_2 purity ≥ 95%, Target recovery ≥90%

1. Patton et al., **2004**, Chem Eng Res Des, 82, 199-209
2. Rezaei and Webley **2009**, Chem Eng Sci, 64,5182-5191
3. Khurana and Farooq, 2016, Chem Eng Sci, 152, 507-515

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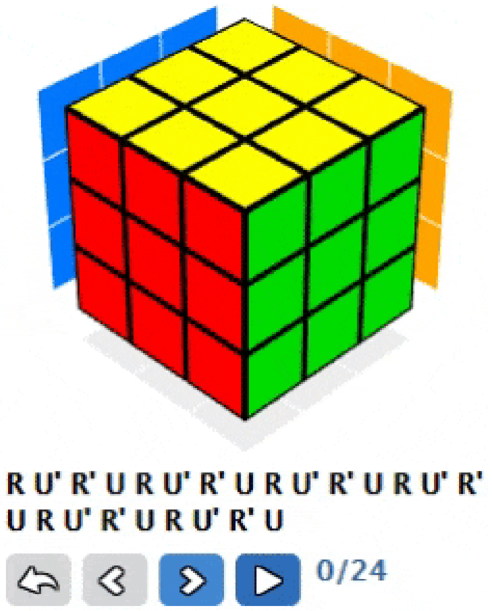
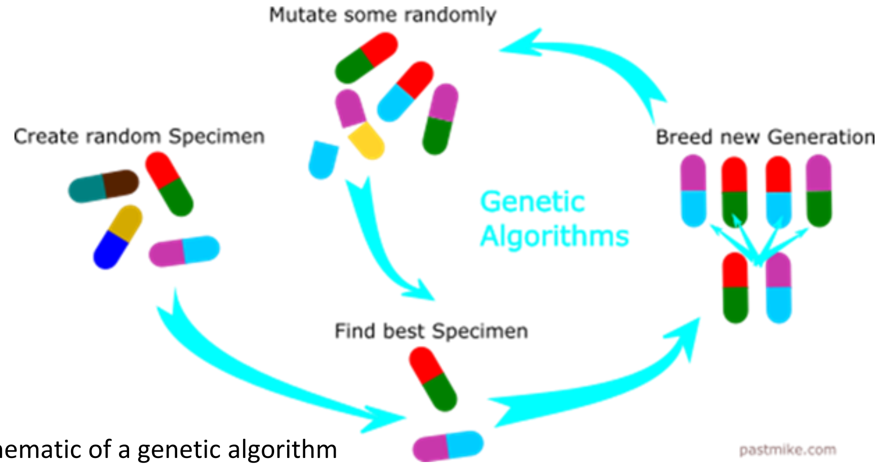
Genetic algorithm





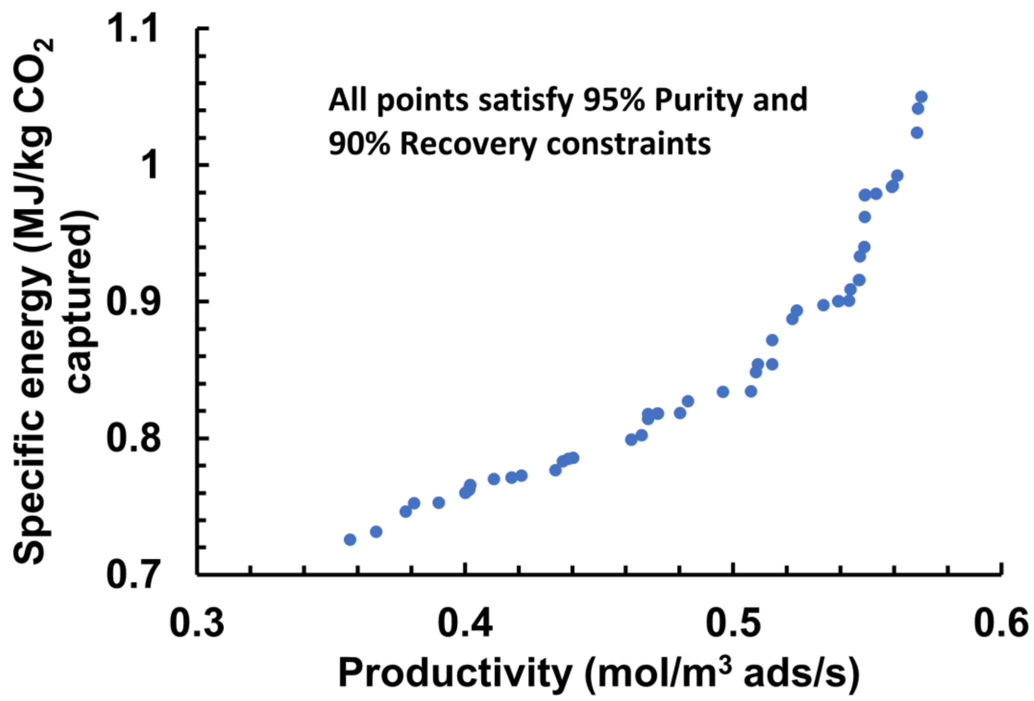
Schematic of a genetic algorithm

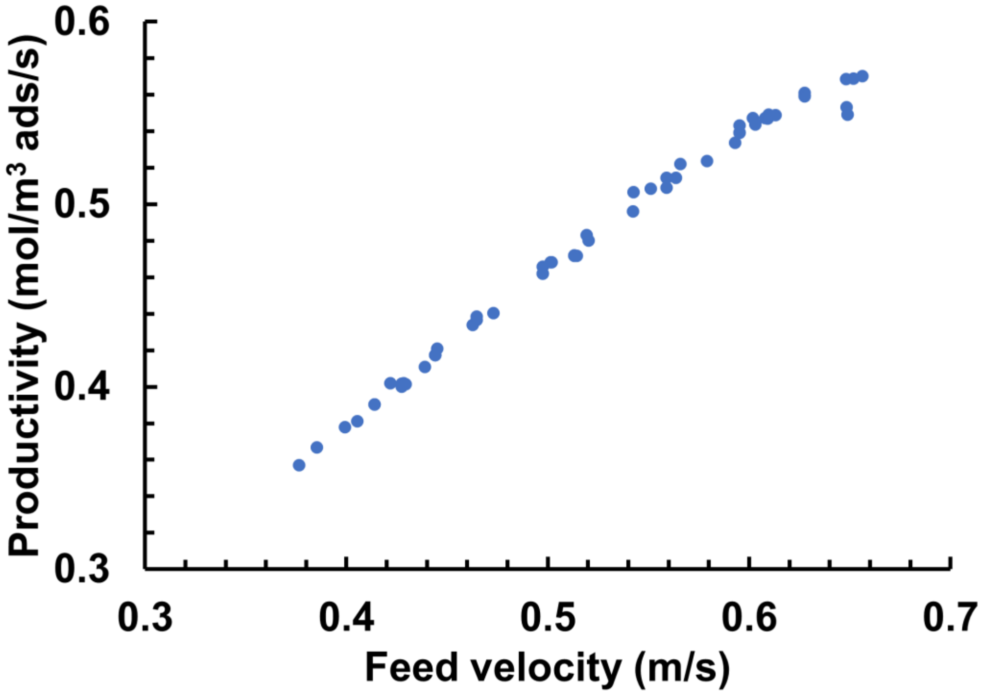
- Multiple variables affect the performance of the adsorption process
- A parametric study may not present the optimum of a process
- Nature inspired algorithms such as genetic algorithms can give the true minimum of the process
- Multiple objectives (Min. specific energy and maximum productivity)
- Specify the bounds of variables (decision variables) that affect process performance and number of simulations needed

  - **Genetic algorithm based optimization (NSGA-II) in MATLAB**
  - **30 generations X 140 populations = 4200 simulations**

https://miro.medium.com/max/384/1*w51Rl6Z6jXHJmeEiLDd_6g.gif

Results from process optimization

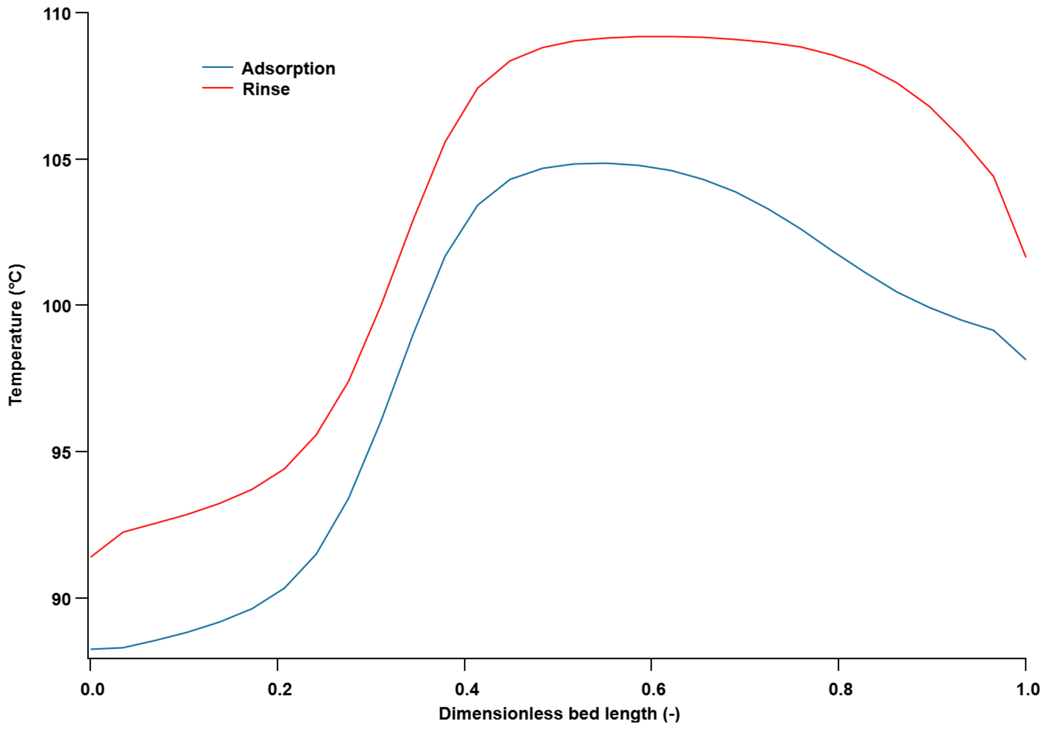




- Minimum specific energy = 0.72 MJ $_{\text{Electric}}$/kg CO_2 captured, Maximum productivity 0.57 mol/m^3 ads/s
- Cycle time = 2.5 – 3 minutes (adsorption step duration =30-40 s)

Conclusions & future work

- **95-90 purity-recovery targets achieved**
- Minimum specific energy = 0.72 MJ $_{Electric}$/kg CO_2 captured
- Maximum productivity= 0.57 mol/m^3 ads/s
- Adsorbent to be "married" to its best cycle to understand true potential : Need for alternative cycle configuration
- Effect of moisture on CO_2 adsorption to be studied
- High temperatures in a cyclic process can affect sorbent stability



Temperature profiles in the column

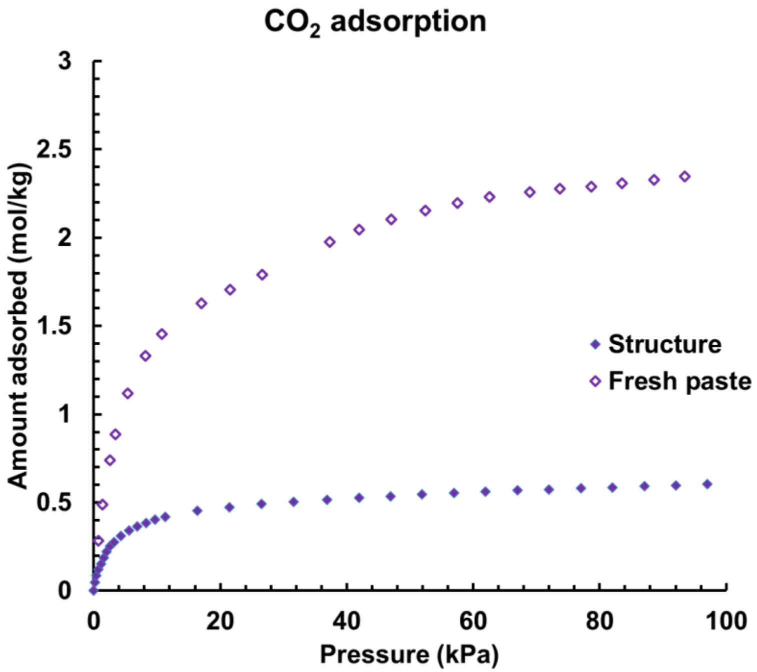
Conclusions & future work

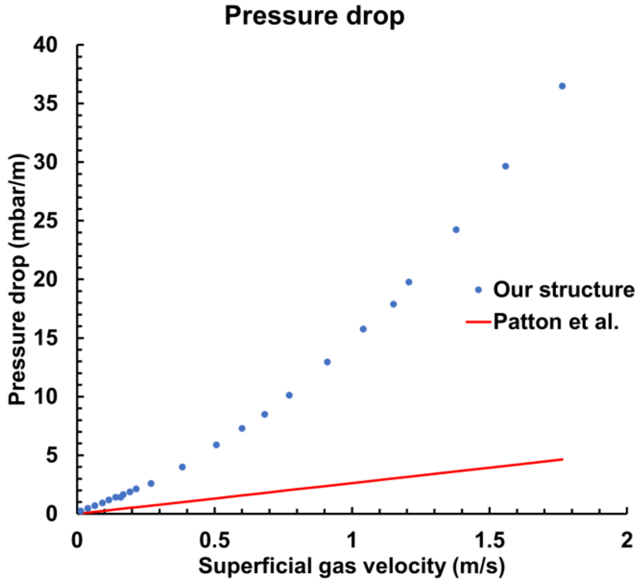
Challenges with 3D printing

- Instability in printing due to phase separation necessitated the use of additives
- Reduction in capacity in comparison with pristine paste
- High shrinkage due to the presence of water

Challenges in the process

- High temperature swings and presence of O_2 can reduce stability of sorbent
- Measured pressure drop higher than predicted pressure drop





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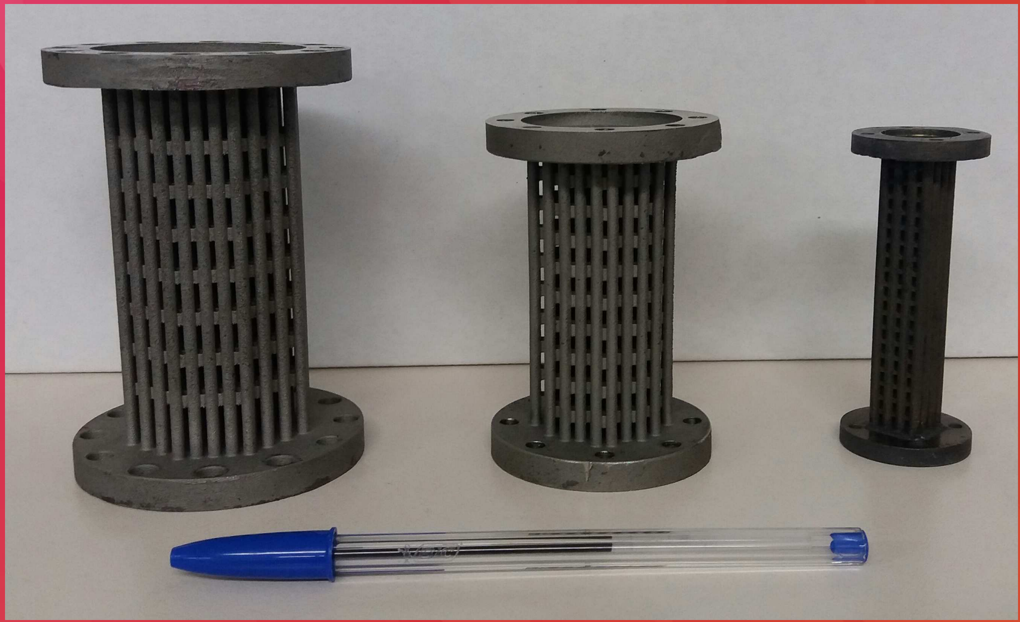
Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760884 (CARMOF).
For more information on this project visit the project web page
https://carmof.eu/

Questions ?

Process intensification in the conversion of CO_2 with a milli-structured reactor



S. Perez, S. Prieto

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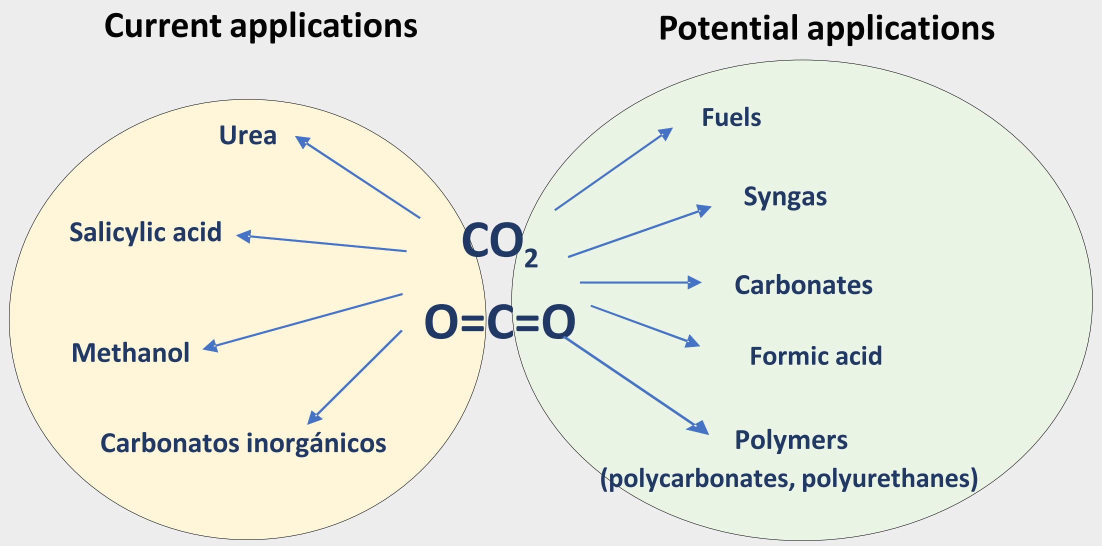
International Workshop on CO_2 capture and Utilization
16-17 February 2021

Outline

1. Process Intensification: microreactors
2. Tecnalia´s millichannel reactor
3. Catalytic tests in Sabatier reaction
4. Millichannel reactor scaling-up
5. Conclusions

1. Process Intensification: microreactors



Current processes:
Poor energy and mass transfer

Process intensification → Microstructured reactor

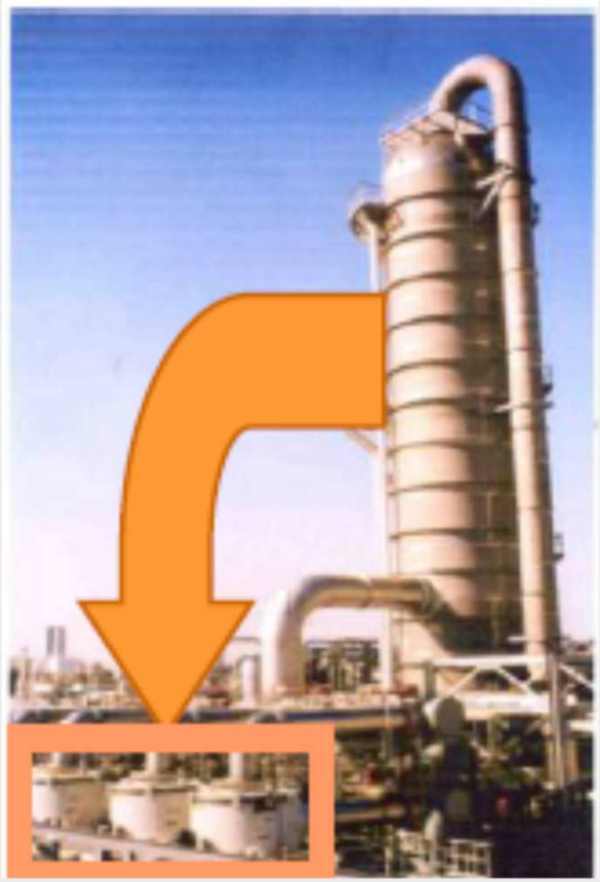
1. Process Intensification: microreactors

What is a micro or a millireactor?

Denomination according to Kiwi-Minsker & Renken (2005):
- 10 - 1000 microns of ID: microchannel reactors
- 1 - 10 millimeters of ID: millichannel reactors

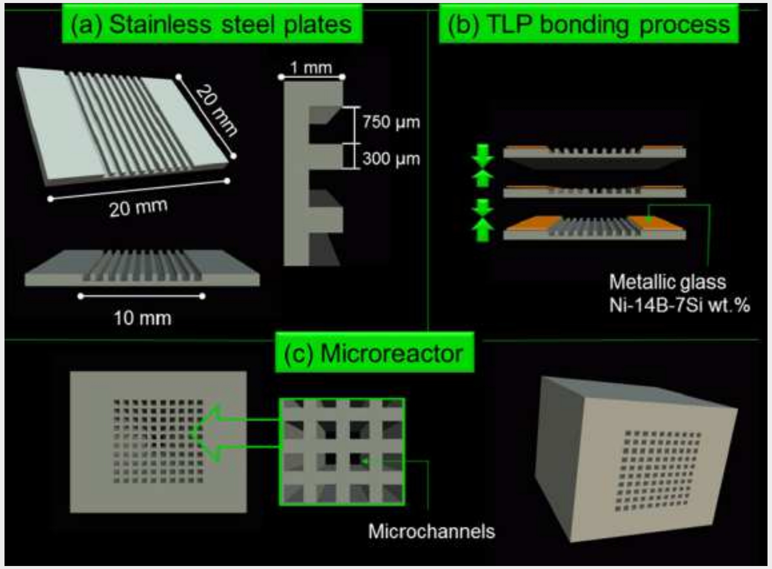
It´s a system to obtain processes:
- more efficient,
- with lower operation costs,
- that generates low amount of waste,
- safer,
- smaller
- and with higher productivity.

In chemical synthesis, the use of millireactors improves the mass and energy transfer between the products and the catalyst.



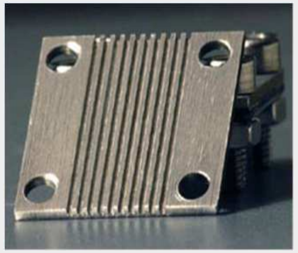
Conventional fixed bed reactor vs 40 times intensified reactor. (Source: Dow Chemical, proceso HOCl)

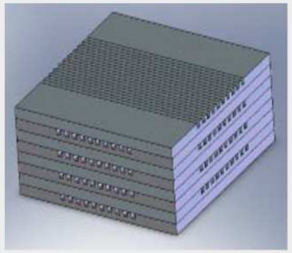
1. Process Intensification: microreactors

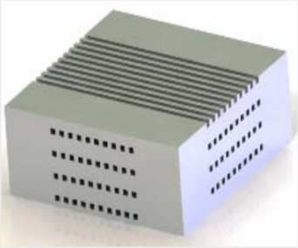


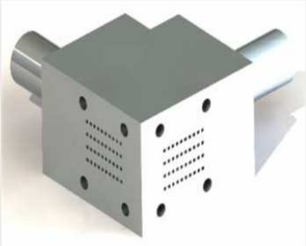
O.H. Laguna et al. / Chemical Engineering Journal 275 (2015) 45–52

Disadvantages:
- Manufacturing method with several phases
- Catalyst deposition
- Scale-up


Micromining

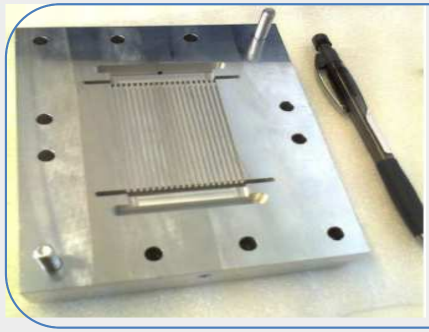

Stacking


Welding


Peripherals

Stages needed for the manufacture of microreactors.
Adapted from *S. Cruz et al. (2011). Chemical Engineering Journal 167. 634-642*

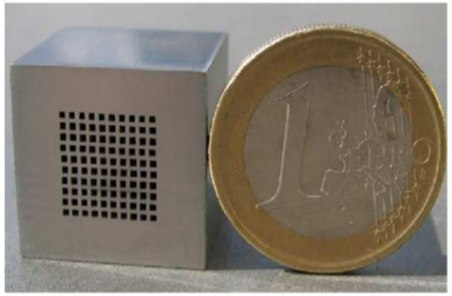
1. Process Intensification: microreactors



Methanol reforming to H2

http://dx.doi.org/10.1016/j.ijhydene.2015.11.047

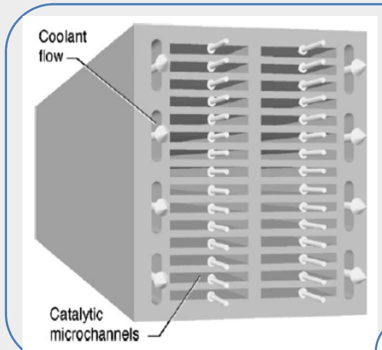
PROX reaction



O.H. Laguna et al. 2011 doi:10.1016/j.cej.2010.08.088

Fischer-Tropsch reaction

Velocys, Inc. 2013



CO2 hydrogenation to methane

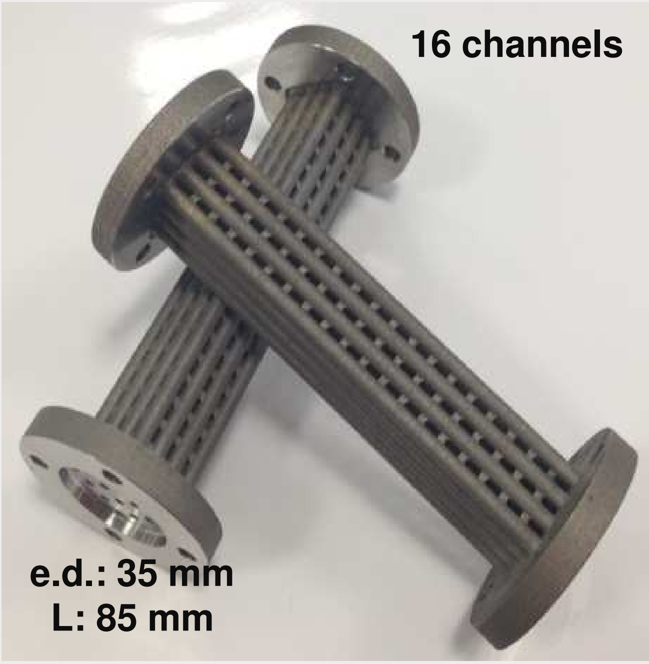
Pacific Northwest National Laboratory USA. *K.P. Brooks et al. Chemical Engineering Science 62 (2007) 1161 – 1170*

Nitrobencene hydrogenation to aniline

www.hzdr.de/db/Cms?pOid=42528&pNid=3367

2. Tecnalia´s millichannel reactor

Based on new additive technologies, Tecnalia R&I has developed a **microstructured reactor** consisting of several tubes with internal diameter in the range of millimeters (1-4) **enhancing both the mass and energy transfer.**



The reactor can be designed and integrated in a pilot plant for a specific process

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EP17382756 (2017) "Method for continuous production of 2,3-butanediol

WO2018/024764A1 "Reactor for Multiphasic reactions"

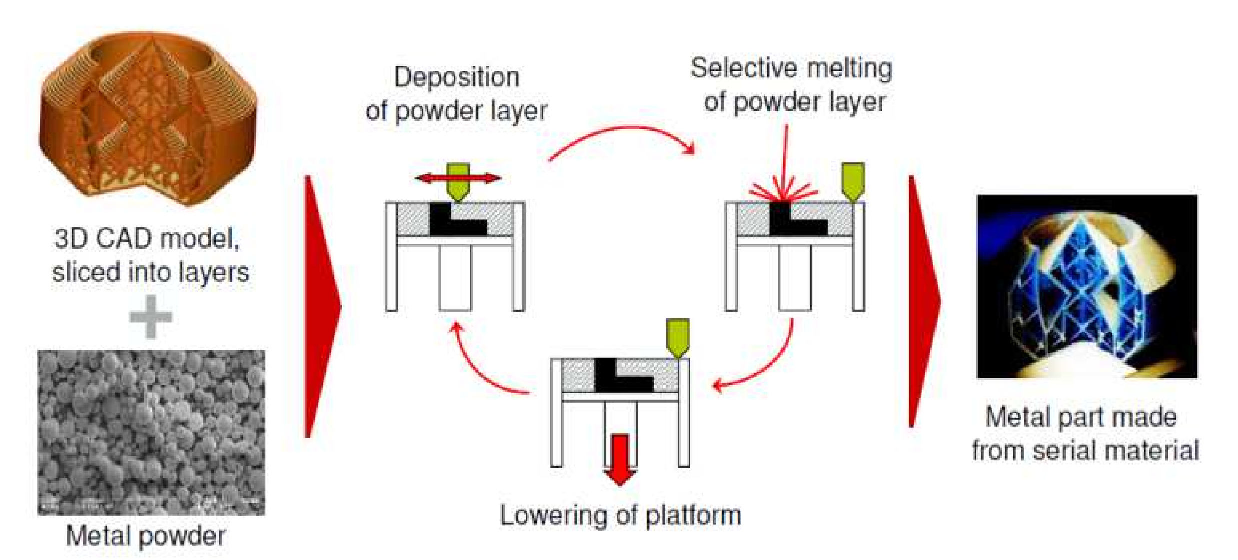
2. Tecnalia´s millichannel reactor

Design features of the reactor

- a high length / diameter ratio
- a good heat transmission / evacuation
- a dimensional uniformity of tubes
- a good thermal and mechanical stability
- a simple manufacture method in one piece, "without layers“
- catalyst filling the tubes

Reactor manufacture

Selective
Laser
Melting



2. Tecnalia´s millichannel reactor

Features	Advantages
Intimate contact between substrates/catalysts	• High mass transfer • Decreases the residence time • Increases 10-20% performance vs conventional reactors
High area/volume ratio	• High heat transfer: **stainless steel AISI 316L** • Minimizes hot spot formation • Limits the propagation of an eventual flame
Low volume	• Savings in production materials, space and energy • Reduced pressure drop
Reduced diffusion distances	• Minimizes hot spot formation • High heat transfer
Scaling-up (not by increasing reactor size)	• Faster implementation of the process on an industrial level • Flexibility to be adapted to the production needs
Thermic fluid introduced through reactor gaps	• Removes heat continuously through the entire reactor • Manages heat in an efficient and flexible way

2. Tecnalia´s millichannel reactor

The millichannel reactor technology is appropriate for **exothermic reactions** and allows to overcome **mass transference** limitations

Our applications

- Hydrogenation
- Butanediol from acetoin (Patented)
- Fischer-Tropsch synthesis
- **CO_2 transformation**

$CO_2 + 4H_2 = \mathbf{CH_4} + 2H_2O$ (RENOVAGAS)

$CO_2 + 3H_2 = \mathbf{CH_3OH} + H_2O$ (LOWCO2)

$2CO_2 + 6H_2 = \mathbf{DME} + 3H_2O$ (CO2FOKUS)

3. Catalytic tests in Sabatier reaction

Comparison traditional fixed-bed vs. millichannel reactor

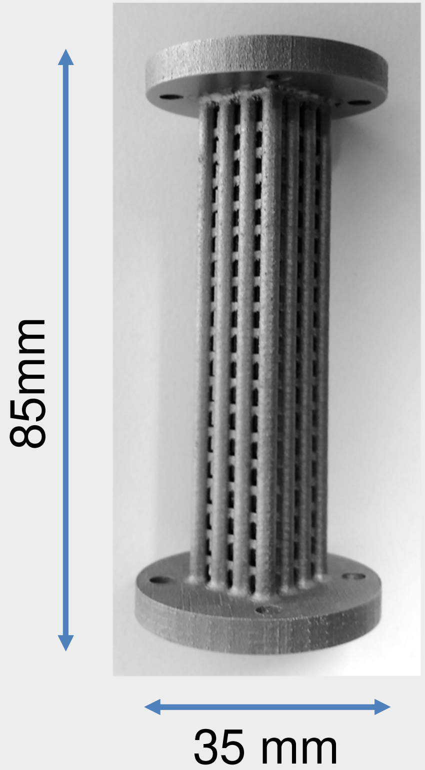
Fixed-bed:

9 mm inner diameter

Millichannel reactor:

16 channels

1.75 mm inner diameter



$CO_2 + 4H_2 = CH_4 + 2H_2O$

CATALYST $Ni/\gamma\text{-}Al_2O_3$	
Metal content (Ni)	25.2 %
Particle size	< 220 µm
Bulk density	0.85 gr/cm^3

REACTION CONDITIONS	
GHSV	80 NL. $g_{cat}^{-1}.h^{-1}$
H_2/CO_2	4
Catalyst mass	2.56 g.

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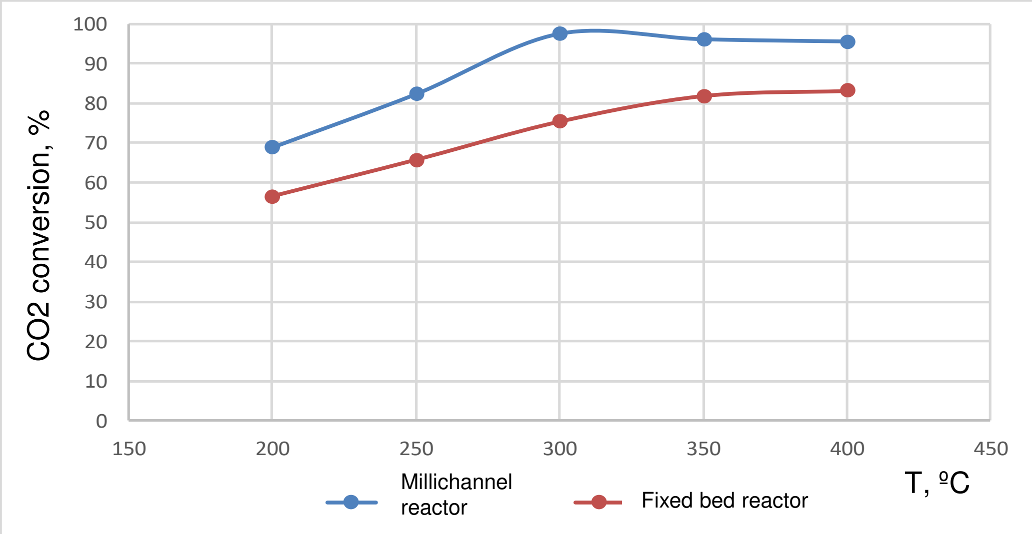
3. Catalytic tests in Sabatier reaction

Comparison traditional fixed-bed vs. millichannel reactor

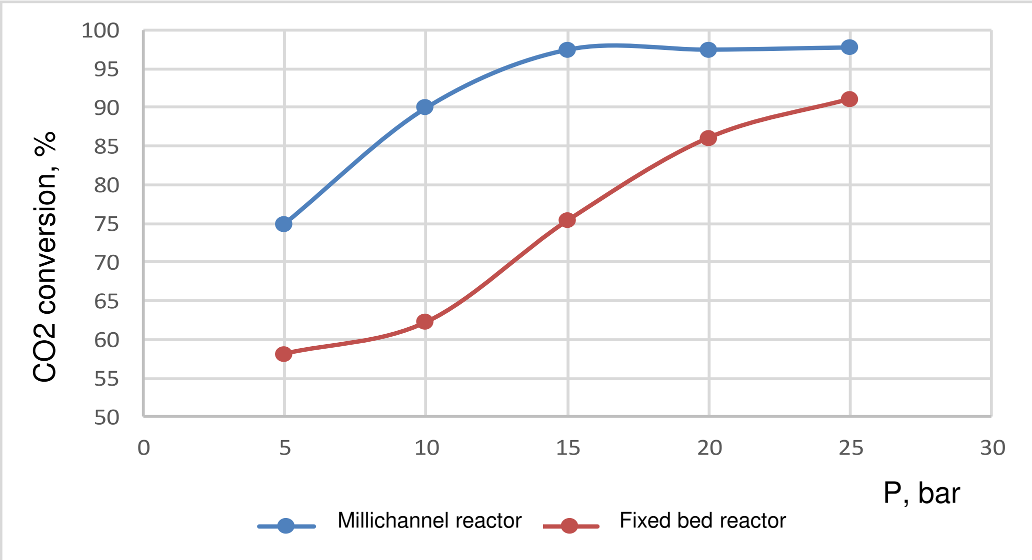
Temperature effect

- At 15 bar



Pressure effect

- At 300ºC



CO_2 conversion increase up to 27,7%

Better mass transfer

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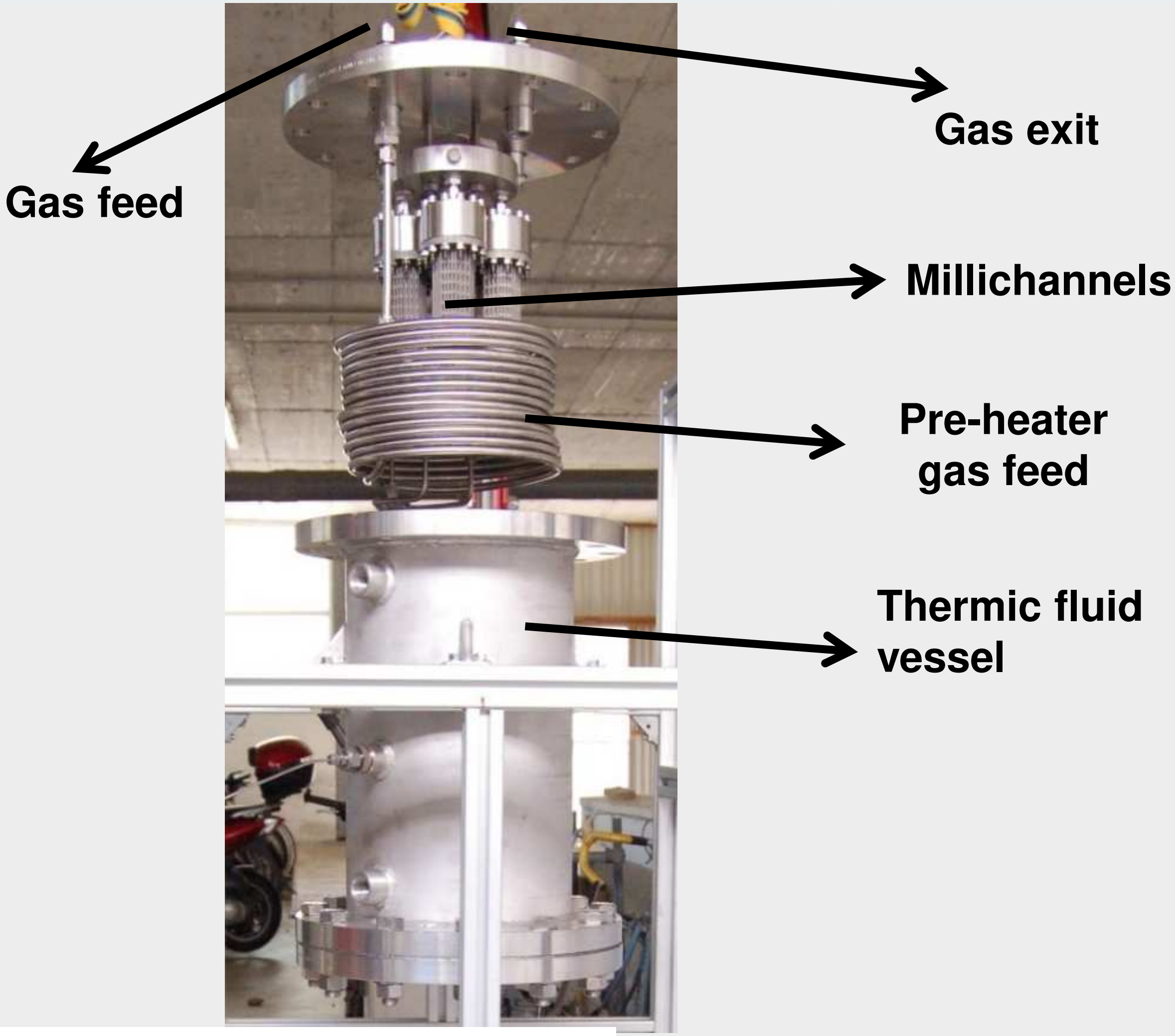
4. Millichannel reactor scaling-up

15kW pilot plant

CO_2 methanation

- Feeding: cleaned biogas
- TRL 5
- Number of channels: 388
- ICP-CSIC catalyst (Ru/CeO_2)

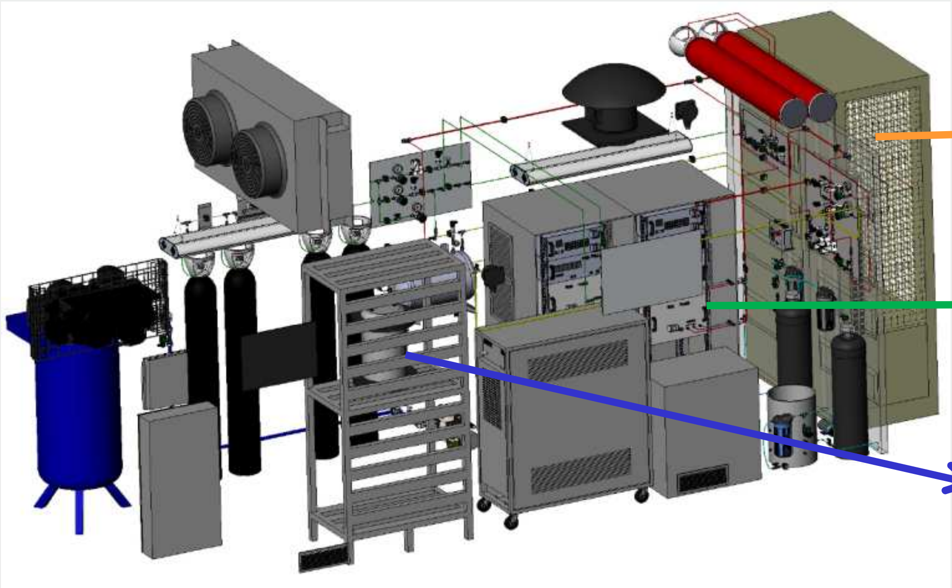


Input			Output		
H_2, %Vol	CO_2, %Vol	CH_4, %Vol	H_2, %Vol	CO_2, %Vol	CH_4, %Vol
53,5	13,4	33,1	2,7	1,7	95,6

RENOVAGAS project,funded by the **Spanish Ministry of Economy and Competitiveness** (MINECO) within the call Retos-Colaboración 2014 (RTC-2014-2975-3).

4. Millichannel reactor scaling-up

RenovaGas



5. Conclusions

- Tecnalia has develop a millichannel reactor for exothermic reactions.
- The reactor:
  - allows a good mass and energy transfer
  - is easy to scale-up by adding channels
  - has a flexible design
  - has a huge number of potential applications
  - has been validated for Sabatier reaction: better results than fixed-bed reactor.

www.tecnalia.com

Thank you for your attention

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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

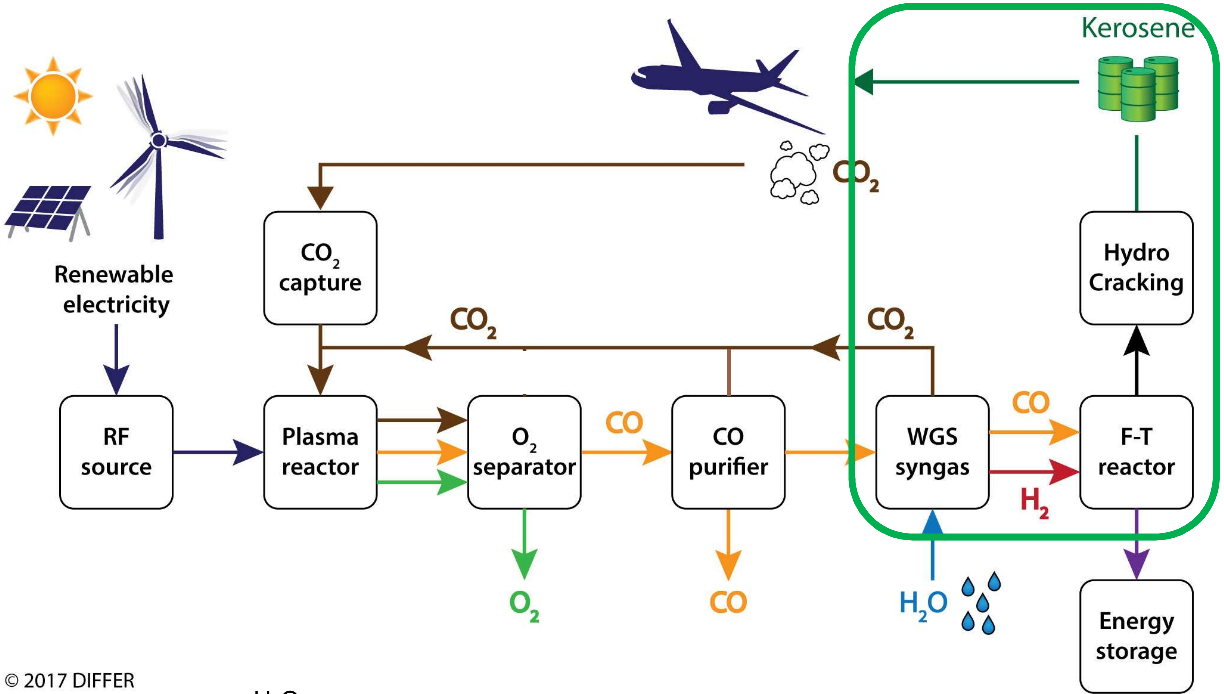
The KEROGREEN syngas route to alternative fuels and chemicals

Francisco Vidal Vázquez (Dr. Sc.)
Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT)

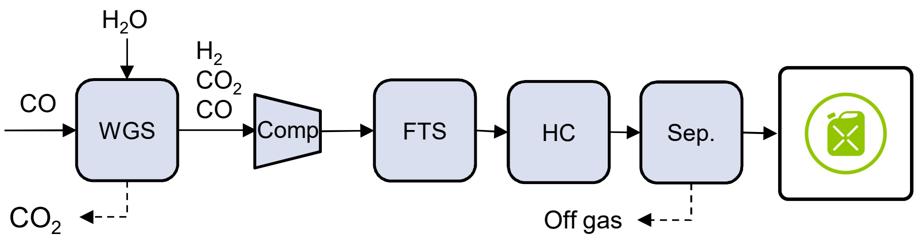
International Workshop on CO_2 Capture and Utilization, 16-17 February 2021, Online Workshop

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

KEROGREEN: CO route to kerosene



© 2017 DIFFER



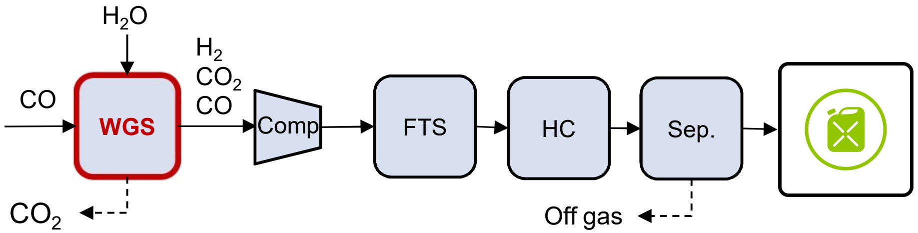
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Syngas Production via Water-Gas Shift (WGS) reaction

- WGS reaction:

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

- Chemical equilibrium:
  - Independent with pressure
  - Favourable at low temperature
- Different catalysts for different temperatures
  - 300 – 400 °C: Fe/Cr-cat (HT-WGS)
  - 200 – 300 °C: Cu/Zn-cat (LT-WGS)



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

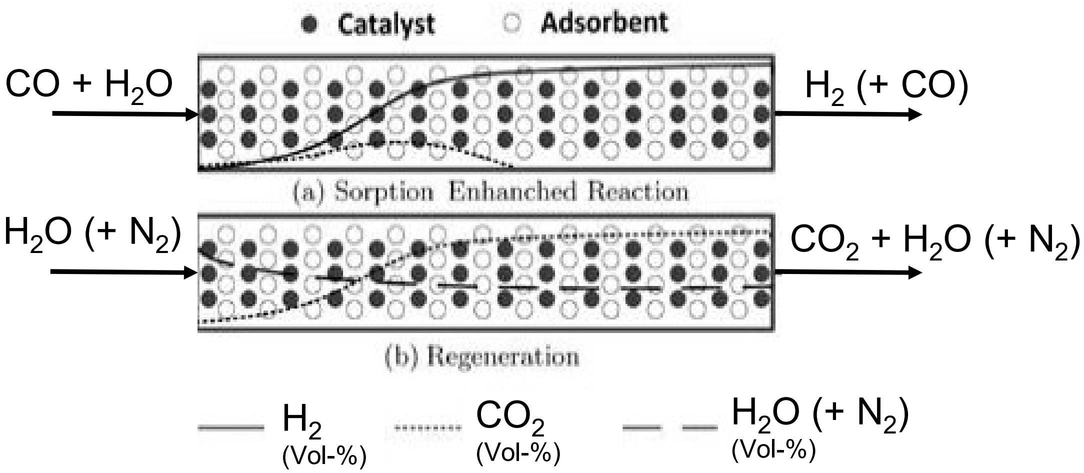
Sorption-Enhanced Water-Gas Shift (SE-WGS)

- SE-WGS:

Sorbent

$$CO + H_2O \rightleftharpoons \cancel{CO}_2 + H_2$$

- Solid sorbent is used for *insitu* CO_2 removal
  - Dynamic operation of reactor
- The sorbent is mixed with the catalyst and placed in the reactor
- Other advantages:
  - Higher conversion
  - Reduction of required steam for the WGS
  - Overall-simplification of the process ($WGS + CO_2$ removal)
  - CO_2 recycle up-stream of the process

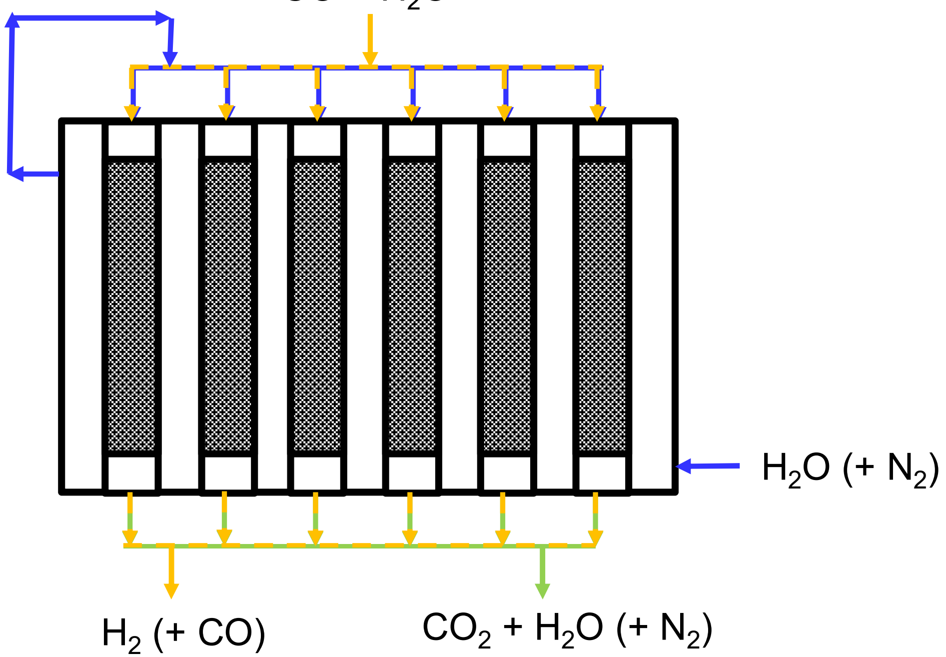


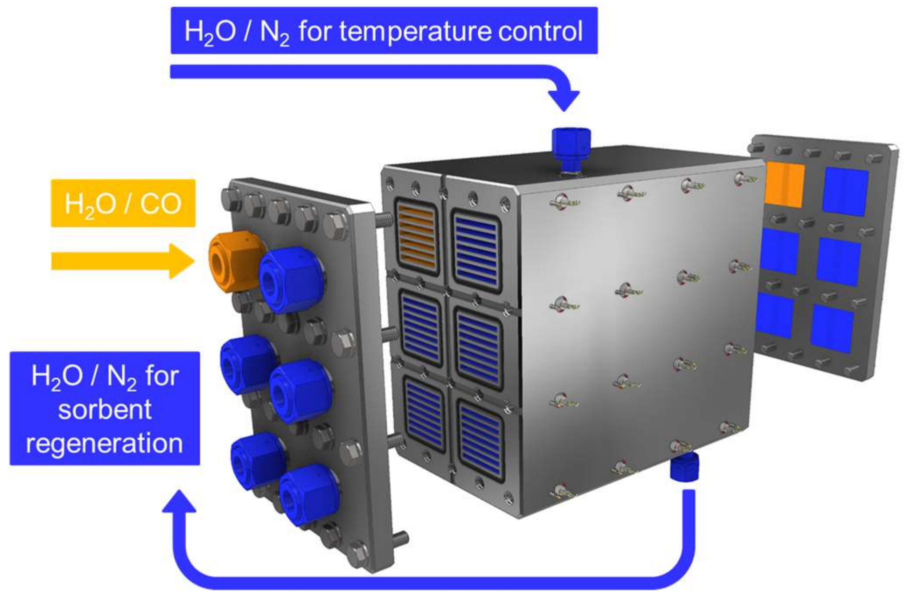
Modified figure from Rodriges et al. 2017

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

SE-WGS reactor for KEROGREEN

- SE-WGS reactor has 6 different beds which are operated dynamically in order to keep constant outlet flow of syngas
  - Cycle of Reaction/Depressurization/Regeneration/Pressurization





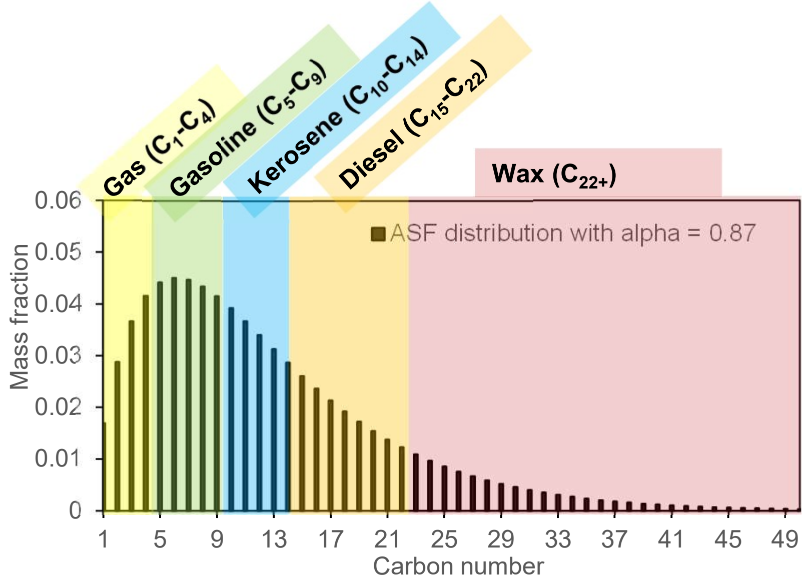
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

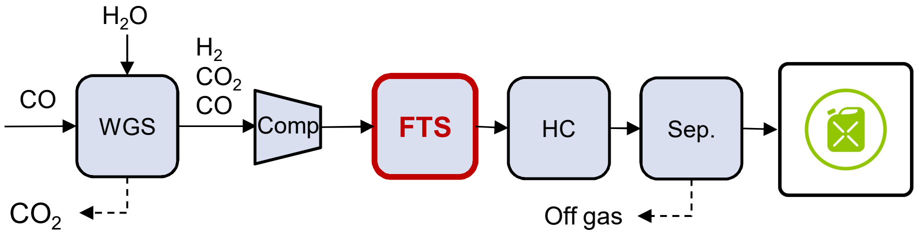
Fischer-Tropsch Synthesis

- Highly exothermic heterogeneously catalysed polymerization reaction

$$n\,CO + 2n\,H_2 \rightarrow (CH_2)_n + n\,H_2O \qquad \Delta H_R^0 = -158\;kJ/mol$$

- Chemical equilibrium:
  - Favourable at high pressure and low temperature
- Different catalysts for different application:
  - 300 – 400 °C: Fe-based cat.
    - Shorter chain hydrocarbons, mainly olefins
  - 200 – 250 °C: Co-based cat.
    - Long chain hydrocarbons, mainly parafins



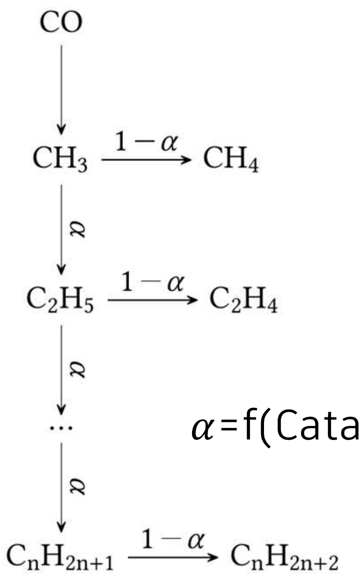


This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

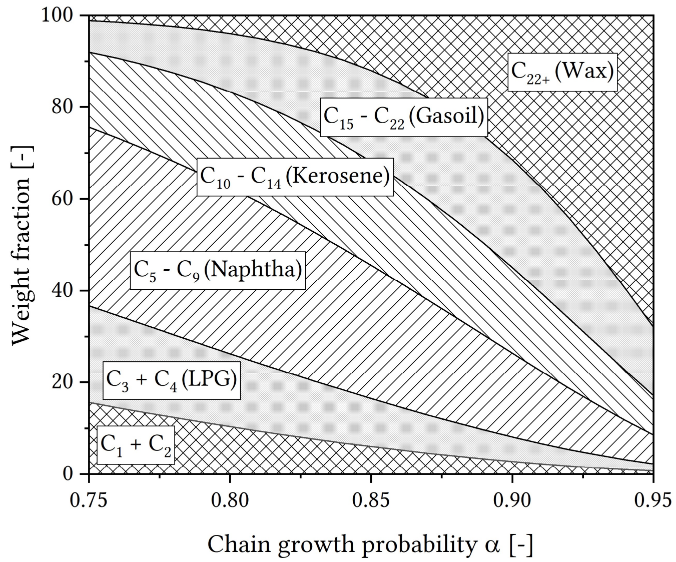
Fischer-Tropsch Synthesis: ASF distribution

- Product distribution can be approximately represented via Anderson-Schulz-Flory (ASF) model – **Chain growth probability**

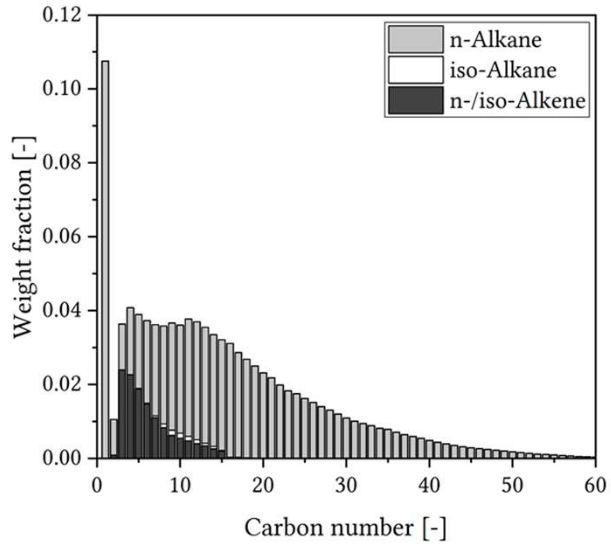
$$W_n = n \cdot (1-\alpha) \cdot \alpha^{n-1}$$



α=f(Catalyst, T, p, …)



Real FTS product composition using Co-based catalyst

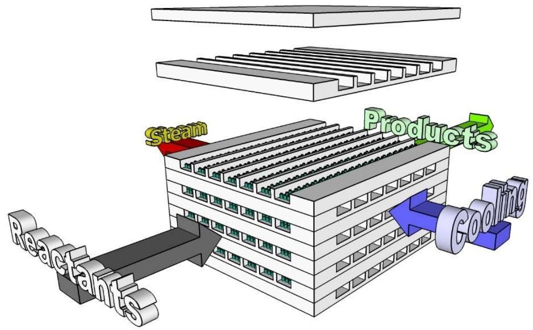


- Higher CH_4 selectivity
- Lower C_2 selectivity
- Olefin formation
- Formation of alcohols (low)

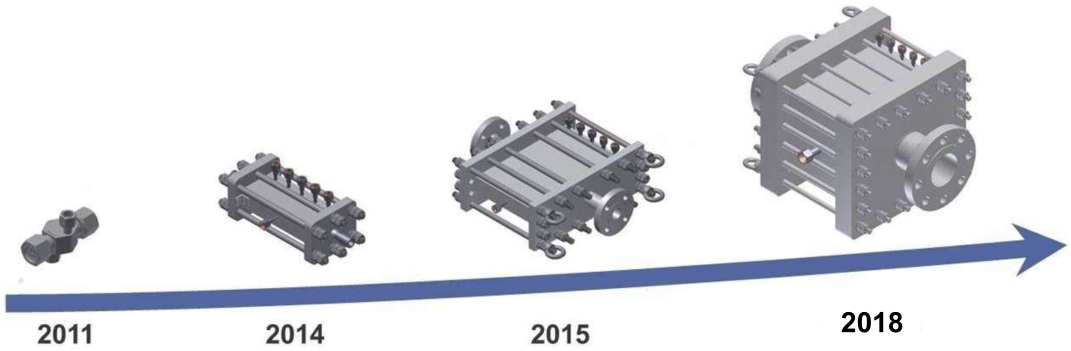
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Fischer-Tropsch Synthesis reactor for KEROGREEN

- Microstructured reactor cooled by water evaporation
  - Compact reactor
  - Excellent control of reaction temperature
  - Good performance at wide range of reaction conditions
  - Good performance under dynamic operation



- Developed at KIT-IMVT → Commercialized and upscaled by INERATEC



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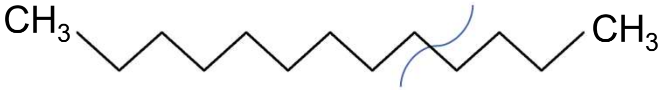
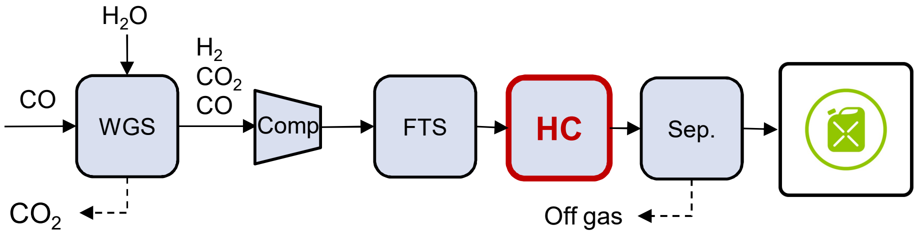
Hydrocracking of heavier FTS products

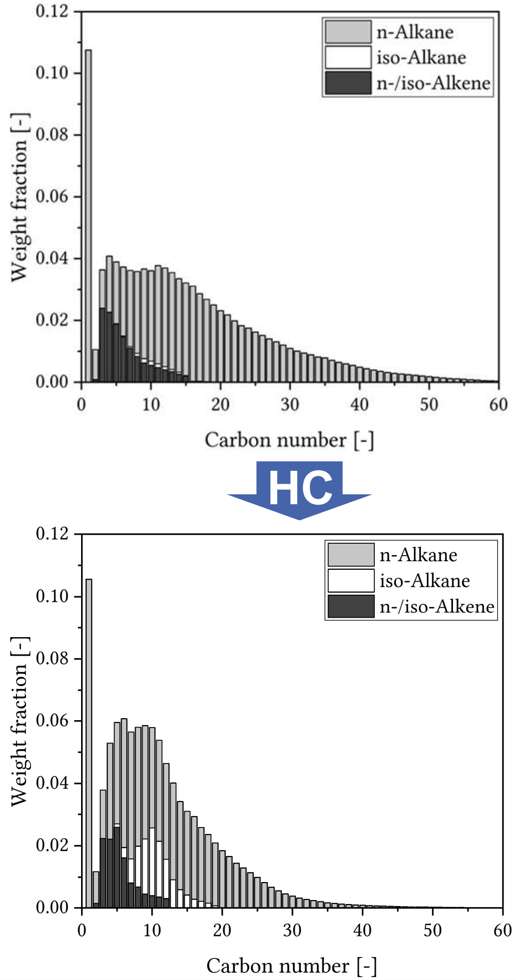
- Hydrocracking (HC) basic example reaction:



$+ H_2 \rightarrow C_xH_y + C_zH_w$

- Typical operating conditions:
  - 250-350 °C
  - 20-50 bar
  - Bifunctional catalyst (Metal/Zeolite)
- Purpose of HC:
  - Increase liquid fuel fraction (remove waxes)
  - Decrease alkene (olefins) content → not applicable to kerosene
  - Increase isomer content → improve cold flow properties

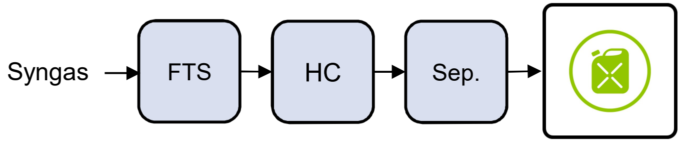




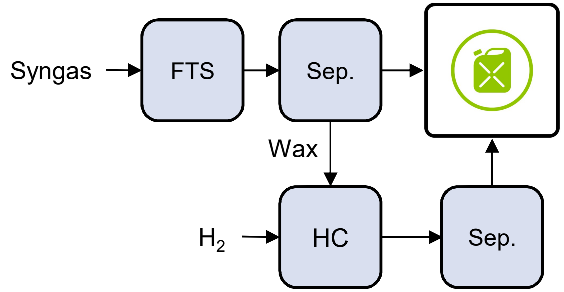
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Hydrocracking of FTS products

- HC general considerations:
  - Partial conversion of waxes (C_{22+}) in order to avoid overcracking
  - Process design considerations:
    - HC of the full FTS outlet:
      - Simpler process configuration
      - Risk of secondary cracking (overcracking) due to CO in the gas phase
      - Cracking of non-wax fraction can happen



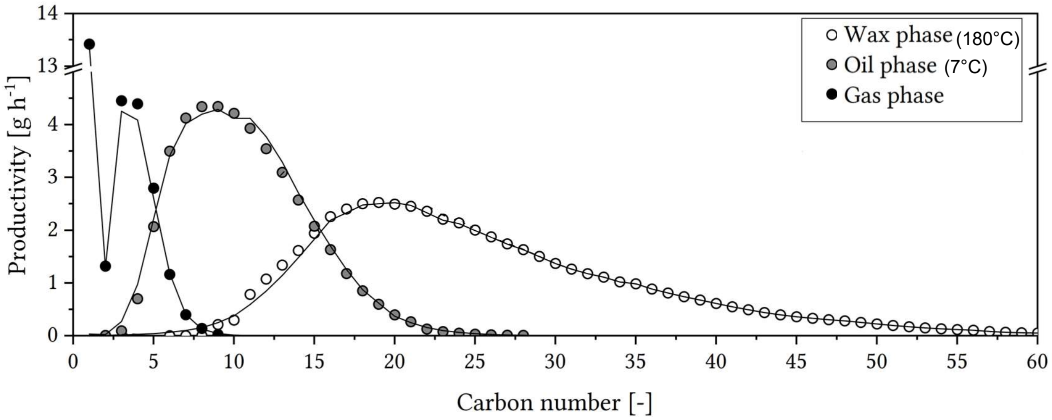
    - HC only of the wax phase:
      - More complex process configuration
      - Pure H_2 to the hydrocracker
      - Better product distribution



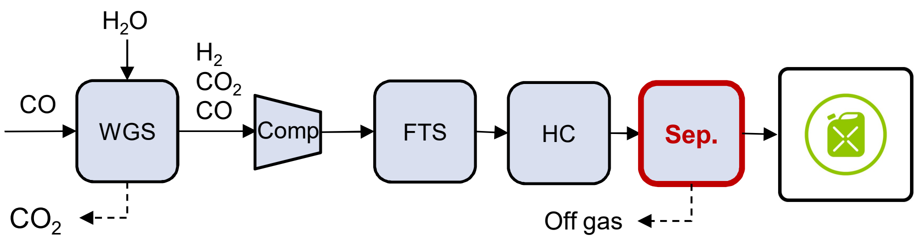
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Product separation

- Flash separation
  - Hot flash (180-220 °C) → Wax product
  - Cold flash (5-10 °C) → Liquid product
  - Rest → Gas phase (Off-gas)



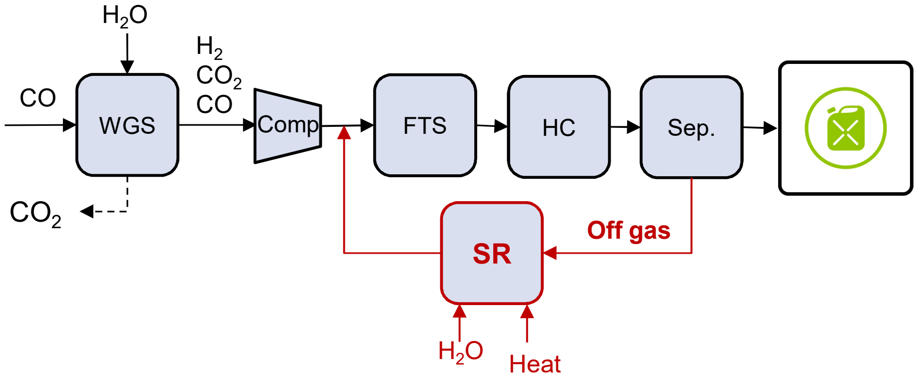
- Distillation is required for sharp separation of product
  - Kerosene grade only achievable by distillation



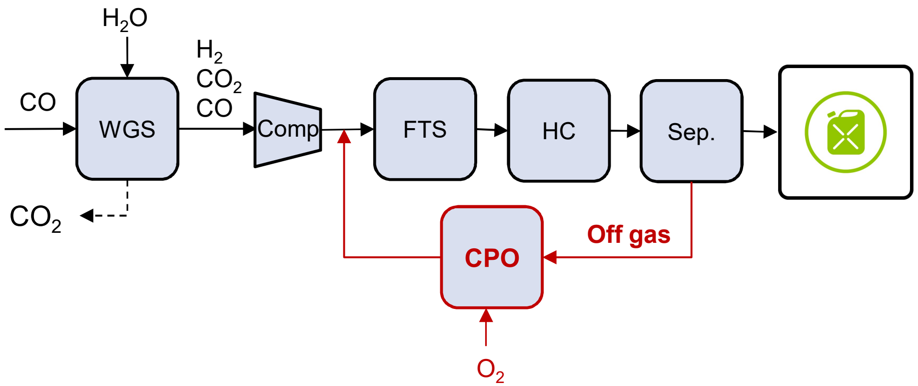
This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under GA-Nr. 763909

Off-gas recirculation

- Off-gas composition → H_2, CO, methane, C_2, C_3, C_4, C_5(traces of C_{6+}), maybe CO_2 too
- Options for off-gas recirculation:
  - Steam reforming (SR)



  - Catalytic partial oxidation (CPO).



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Summary and conclusions

- Conclusions
  - Not full selectivity to kerosene can be achieved (< 50 %)
    - However, other valuable products such as gasoline, diesel and waxes are obtained.
    - Isomerization stage still might be required to achieve fuel grade

- Other general considerations for process integration
  - Heat and material integration between the different components of the KEROGREEN plant is crucial for maximizing energy and carbon efficiencies
  - Maximize energy and carbon efficiency
    - Difference when using fossil fuels as raw material. Cost structure changes (more OPEX) and plant size changes
  - Techno-economic and LCA analyses are the ultimate test to decide what could be the best option

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

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Karlsruher Institut für Technologie

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Georg Rabsch
Lucas Brübach
Hannah Kirsch

THANK YOU FOR YOUR ATTENTION

RELATED PUBLICATIONS

T. J. Stadler, P. Barbig, J. Kiehl, R. Schulz, T. Klövekorn, and P. Pfeifer, "Sorption-Enhanced Water-Gas Shift Reaction for Synthesis Gas Production from Pure CO: Investigation of Sorption Parameters and Reactor Configurations," *Energies*, vol. 14, no. 2, p. 355, 2021

H. Kirsch *et al.*, "CO2-Neutral Fischer-Tropsch Fuels from Decentralized Modular Plants: Status and Perspectives," *Chemie-Ingenieur-Technik*, vol. 92, no. 1–2, pp. 91–99, 2020

KEROGREEN

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

INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILIZATION

TU/E - EINDHOVEN - 16-17 FEBRUARY 2021

Session 3B (chairperson Oana David)	
11:45-12:05	Msc. A. Sliousaregko - Industrial membrane requirements for CO_2 removal from different gas mixtures - Current practices and developments
12:05-12:25	Dr. I. Kim - Technologies demonstration in REALISE
12:25-12:45	Mr. Paul Cobden and Prof. C. Abanades - Pilot preparation for demonstration in the C4U project
12:45-13:05	Mr. T. Swinkels - Decentralized FA based power generators
13:05-13:25	Dr. L. Roses - Design and development of a membranebased post-combustion CO_2 capture system

ORGANIZED BY

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Industrial membrane requirements

for CO_2 removal from different gas mixtures -

Current practices and developments

Anastasia Sliousaregko, R&D Process Engineer, asliousaregko@dmt-et.nl

Yndustrywei 3, 8501 SN Joure, Netherlands

dmt International

Who are we?

Our mission: to create a clear and prosperous future

- Engineering firm specializing in biogas upgrading and gas desulfurization
- Over 150 references and more than 30 years of experience
- Global provider of solutions that help build a sustainable future
- Award-winning portfolio

Biogas Upgrading — Carborex® MS

Gas Desulfurization — Sulfurex®

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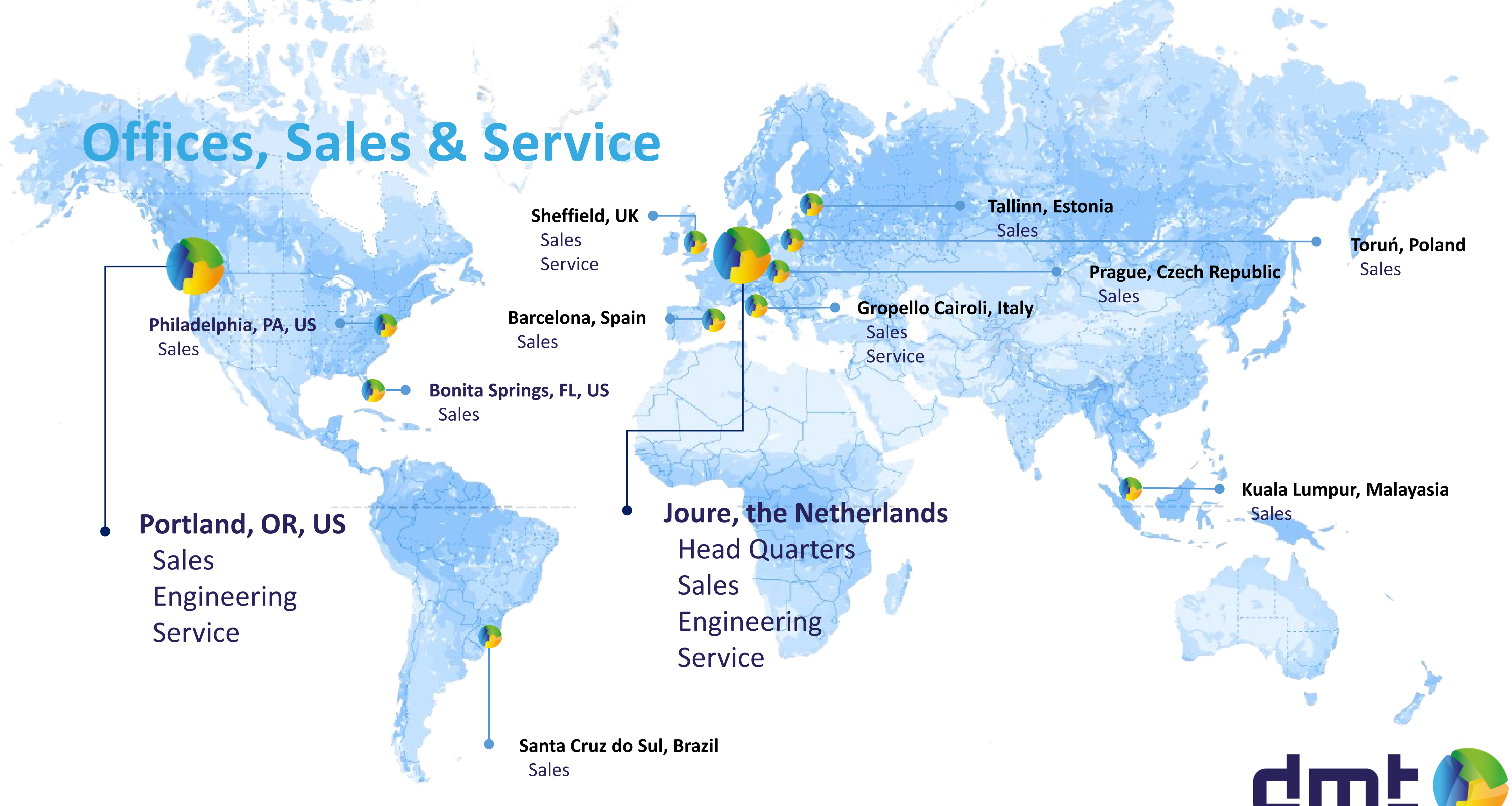
Offices, Sales & Service



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Membrane industrial requirements

Post-combustion flue gas capture

Natural gas sweetening

Biogas upgrading

For the full state-of-the-art report

Bio Co Mem

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Post-combustion flue gas capture

Membrane industrial requirements

Mitigation of CO_2 emissions with (CCS)

- Insufficient incentive for the industrial parties
  - Costly overall process (capture, transport and storage)
  - DAC at low TRL. Delocalized emitters are more expensive
  - CO_2 capture range of 35-60 €/ton higher than EUA of 25-40 €/ton
- CO_2 separation techniques
  - Chemical/Physical absorption (Amines as ref.)
  - Membrane separation
  - Adsorption-absorption by solid materials
  - Calcium Looping
  - Cryogenic distillation

Petra Nova, Texas US (2016-2019), Amine absorption commercial plant

Industrial requirements

- 4-20% CO_2 ingas from power generator
  - Low/Atmospheric pressure
  - Vapour, O_2, SO_x, NO_x, NH_3, …
  - High flows 40,000 Nm^3/h
- To be competitive with amines or 90% CO_2 capture for installed prices not less than 50 €/m^2

Specifications	Value	Unit
P_{CO2}	>2,250	GPU
CO_2/N_2 selectivity	>30	---
Temperature	100	ºC
Design pressure	7	bar
Costs	< 100*	€/m^2

*Target set by the BioCoMem project

Haibo Zhai (2019)

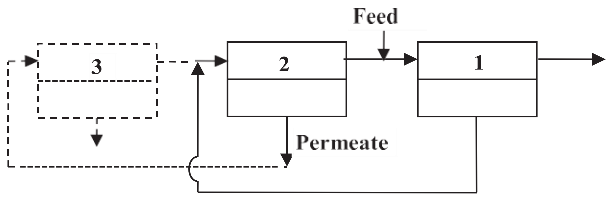
Other requirements

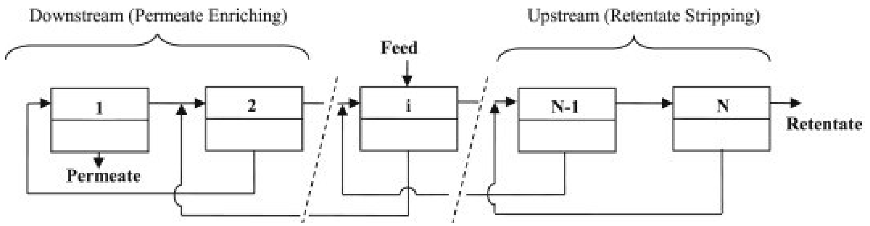
- Compatibility and stability
- Lifetime
- Fabrication and packaging
- Fouling

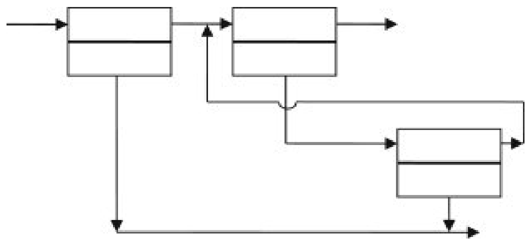
Membrane-based PCC

- PIM, PEO, TR, PI – high performance polymeric-based membranes
- FSC pilot testings
  - promising under humidified conditions (5 m^3(STP)/(m^2·h·bar) and $CO_2/N_2 > 500$), NTNU

Configurations







Kalipour et al (2015)

Natural gas sweetening

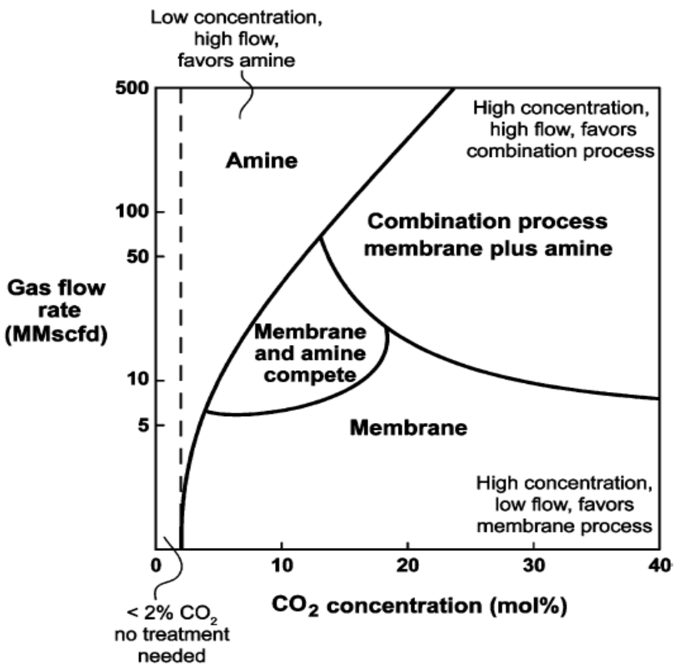
Membrane industrial requirements

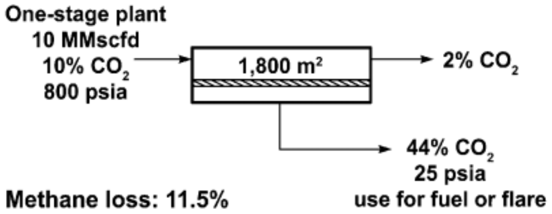
Current practices

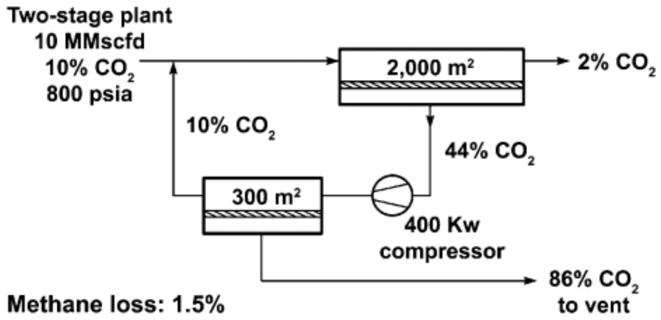
- Amine scrubbing (higher flows, lower CO_2 concentrations)
- Membrane separation (5-10% market share)
  - Polymeric: CA, PA, PI, perfluoro-polymers
  - Silicone composite
  - Hybrid amine membranes

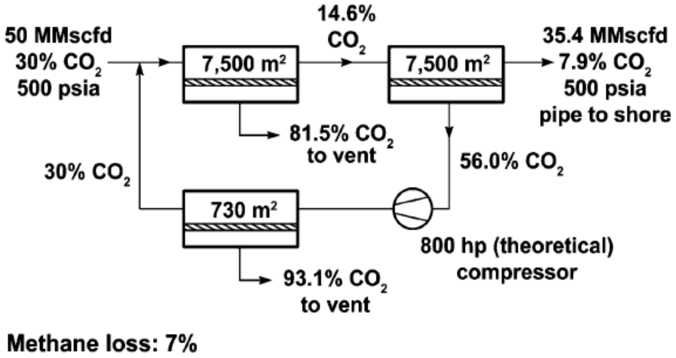
Configurations

- Pretreatment (plasticization)
  - (aromatics, heavy hydrocarbons, oil mist and particulates)
- 1-stage (gas-wells), 2-stage (higher stream) and 3-stage (off-shore)









Baker, Lokhandwala (2008)

Industrial requirements

- From ~8% CO_2/ 80% CH_4
  - H_2O, N_2, H_2S
  - 20,000 - 200,000 Nm^3/h
  - Atmospheric pressure
- Grid quality
  - H-gas: > 96 vol% CH_4
  - L-gas: 88-92 vol% CH_4
  - Other parameters
    - WI, calorific value, total sulfur, etc
- Permeance and module size
- Asymmetric hollow fibers
- 4 – 12'' module diameter

Network	Gas	Pressure	Pressure (Netherlands)
HTL	G-gas and H-gas	usually > 16 bar	> 45 bar(a)
RTL	Mostly G-gas	about 4-16 bar	11 – 40,5 bar(a)
RNB	Mostly G-gas	< 4 bar	9 / 4 / < 4 bar(a)

Sweet natural gas	Value	Unit
P_{CO2}	> 100*	GPU
CO_2/CH_4 selectivity	50*	
CO_2	<2,5	%
Temperature	5-30	ºC
Design pressure	Depends	bar

*Target set by the BioCoMem project

For H-gas grid 80% removal efficiency

State-of-the-art materials

- Polymeric (PEBA, PEO-based)
- Facilitated transport
- Composites (Mixed-matrix membranes)
- Carbon molecular sieve

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Biogas upgrading

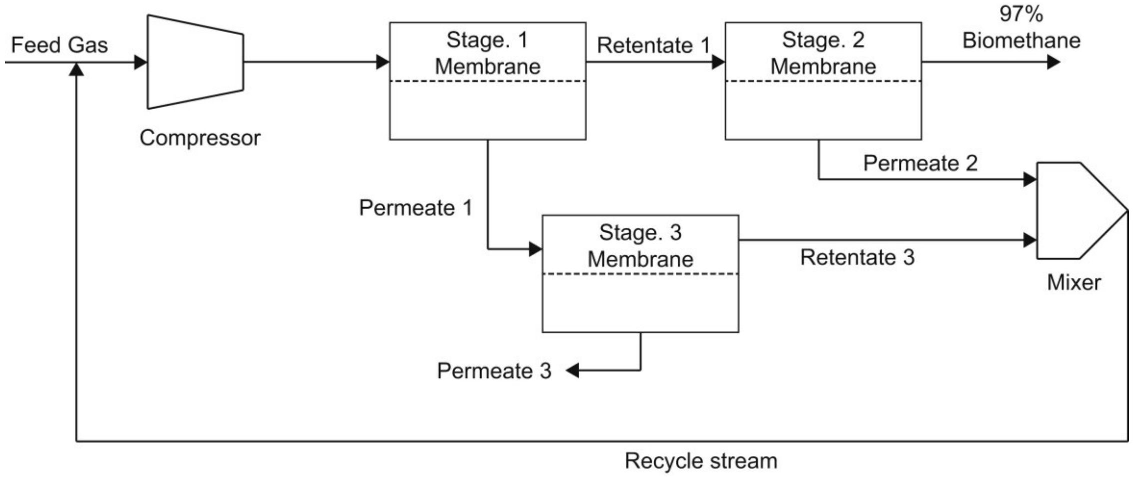
Membrane industrial requirements

Current practices

- Water scrubbing
- Membrane separation (36% market share by 2025)
  - Industrially dominant polymeric membranes: CA, Psf, PI
- Chemical scrubbing
- PSA

Configurations

- CH_4 recovery
- Specific energy
- Specific area
- Cost
- Pressure
- Pretreatment



✓2-stage – 2-4% CH4 slip*
✓3-stage – 0,5-1% CH4 slip*
*Depending on the membrane supplier

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Industrial requirements

- From ~**45% CO_2/ 55% CH_4**
  - H_2S, siloxanes/VOC, NH3, H_2O
  - 50 - 5,000 Nm^3/h
- Selectivity
- Grid quality
- Hollow fiber and spiral-wound
- 4 – 8’’ module diameter

Biogas upgrading specifications	Value	Unit
P_{CO2}	50-100	GPU
CO_2/CH_4 selectivity	50	
CH_4 slip	<0.5	%
Temperature	55	ºC
Design pressure	14-20	bar

For H-gas grid 90% removal efficiency – depending the supplier

State-of-the-art materials

- Composites
- MOF
- FSC

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Thank you for your attention!

Any questions?

International

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INTERNATIONAL WORKSHOP ON CO_2 CAPTURE AND UTILIZATION
TU/E - EINDHOVEN - 16-17 FEBRUARY 2021

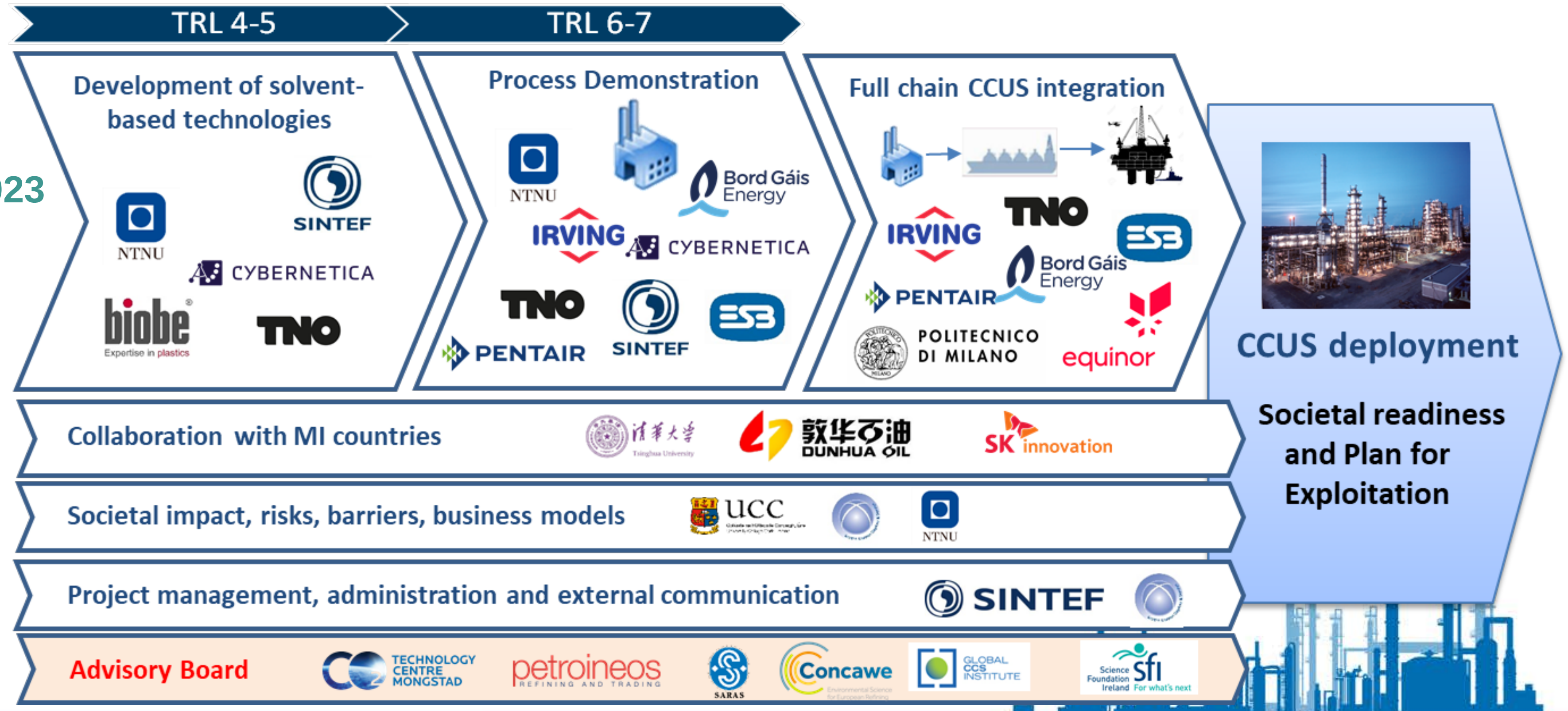
REALISE CCUS

Technologies demonstration in REALISE project

Inna Kim (SINTEF) and Juliana Monteiro (TNO)

Demonstrating a refinery-adapted cluster-integrated strategy to enable full-chain CCUS implementation - REALISE

- **Project period: 05.2020 - 04.2023**
- **Project partners:**
  - 14 EU partners
  - 2 partners in China
  - 1 partner in S. Korea
- **Project budget: 7 MEuro**



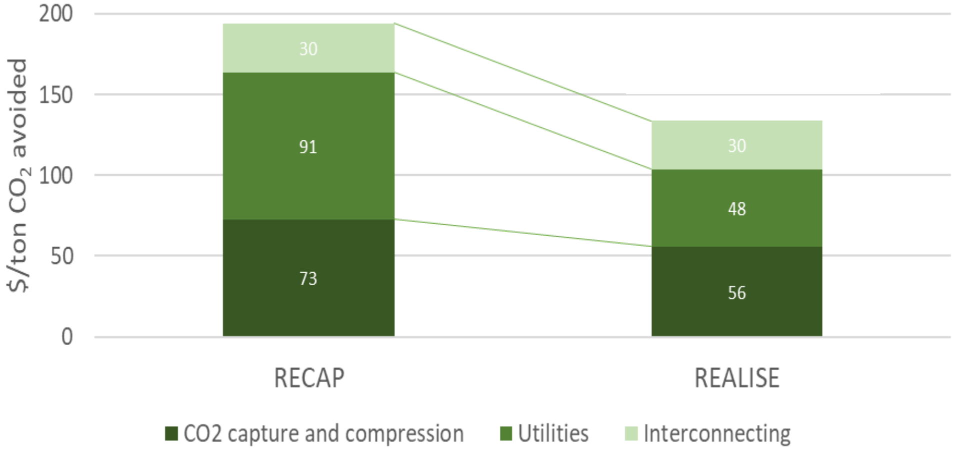
REALISE objectives

Reduction of GHG emissions

Increase of cost- and implementation- effectiveness

- Using low-energy HS-3 solvent ➔ decrease of the energy demand of CO_2 capture by 30%
- Maximization of performance thanks to efficient solvent management ➔ active component losses decreased by >80%
- Use of plastic equipment ➔ lower CO_2 capital costs by 15%
- Coupling of available facilities with the power sector ➔ lower the capture costs by at least 30%
- Safe, flexible and guided-choice regarding CO_2 capture scenarios thanks to an open-access simulation tool

Projection of cost reduction for retrofitting CO_2 capture to refineries



"Utilities" include steam demand in the capture plant;
"Interconnecting" means integration of capture plant with both refinery and power plant

REALISE Innovation	Type of reduction	Reduction in capture costs	
		$ / ton $_{CO2\ avoided}$	%
Use of plastic as packing material in the absorber	CAPEX	8	4
Reduced degradation by using DORA and IRIS	OPEX	8	4
Sector coupling and optimal integration and operation	CAPEX and OPEX	24	12
Novel free-to-operate solvent with low energy requirement	OPEX	20	10
TOTAL		60	30

REALISE methodology for scaling up and demonstration of carbon capture and solvent management technologies from TRL 4-5 to TRL 6-7

Lab scale optimization and validation of technologies (WP1)

Validated tools, solvent

Demonstration of carbon capture and solvent management technology (WP2)

Degraded solvent

Full-height pilot plant test with simulated flue gas

CO2

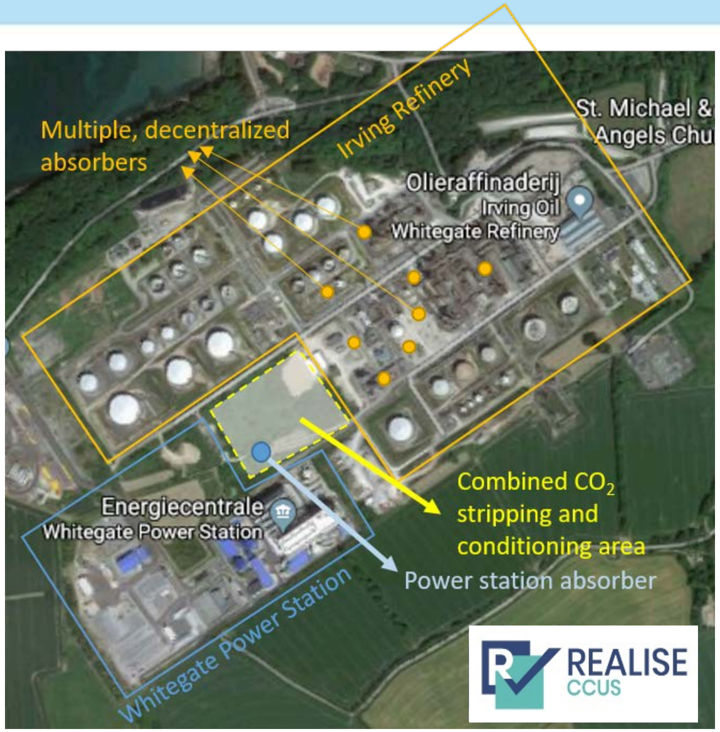
Energy consumption and emission data and data on quality of liquefied CO2

REALISE innovations

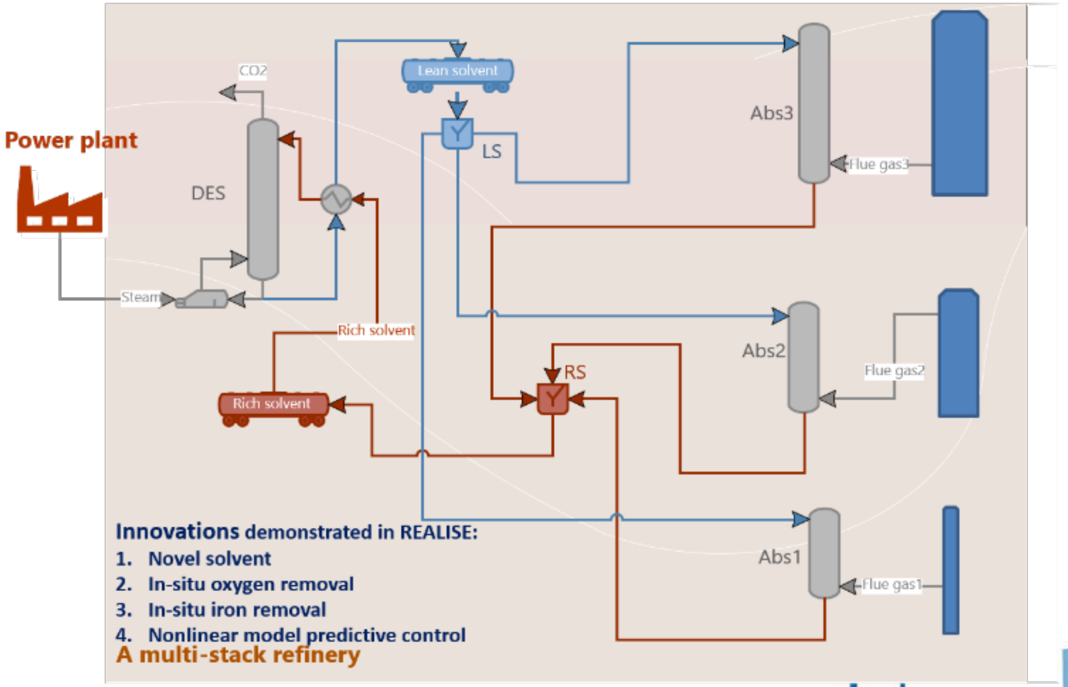
- Novel low energy solvent for CO_2 capture from different flue gases
  - Free-to-operate CO_2 capture solvent developed by NTNU and SINTEF (FP7 HiPerCap)
- Solvent management (to reduce solvent degradation and emissions):
  - Oxygen removal, DORA (patented by TNO)
  - Iron removal, IRIS (patented by TNO)
  - Plastics as material of construction, packing, etc.
- Process integration
  - Nonlinear model predictive control (NMPC developed by SINTEF and Cybernetica)
  - Open-access simulation tool for assessing CO_2 capture strategy at refineries
- Social studies
  - Education and Public Engagement program (Univ. Colledge Cork, see presentation by Dr. Niall Dunphy)

DORA prototype
(TNO)

Multi-absorber concept in REALISE

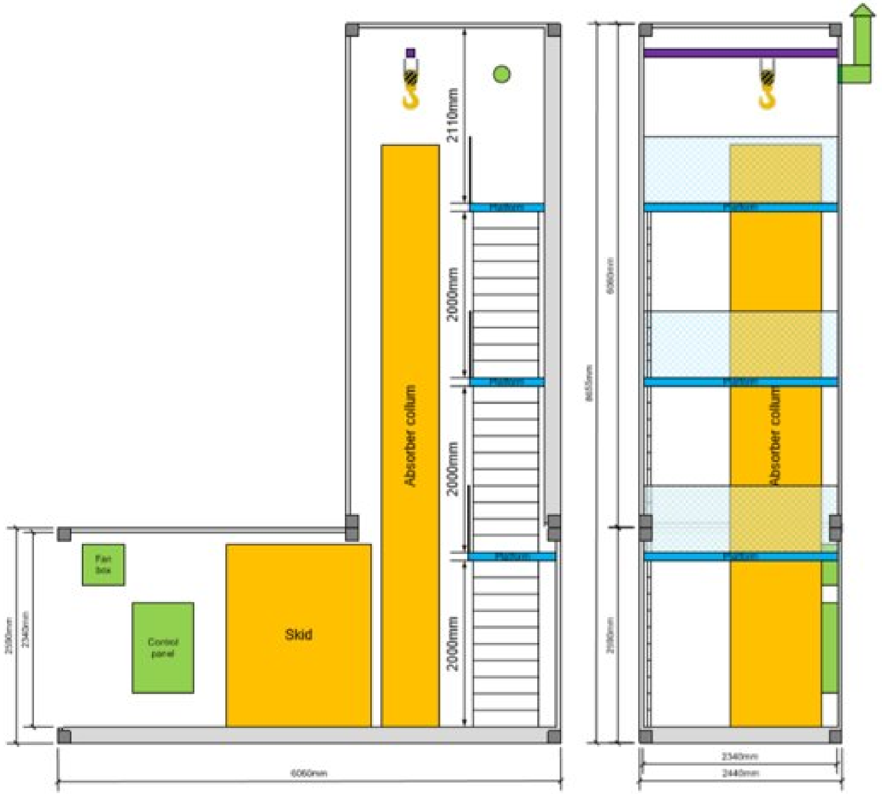


REALISE sector-coupling concept for Irving Oil Whitegate refinery and power stations in Cork, Ireland

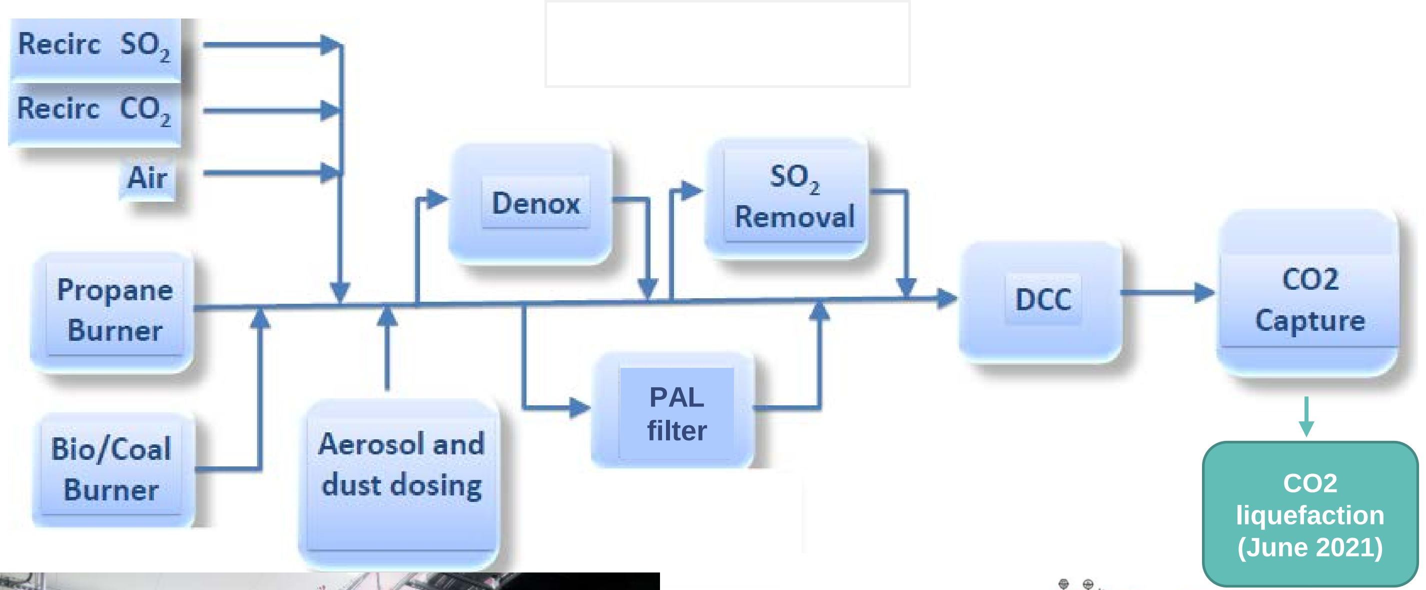


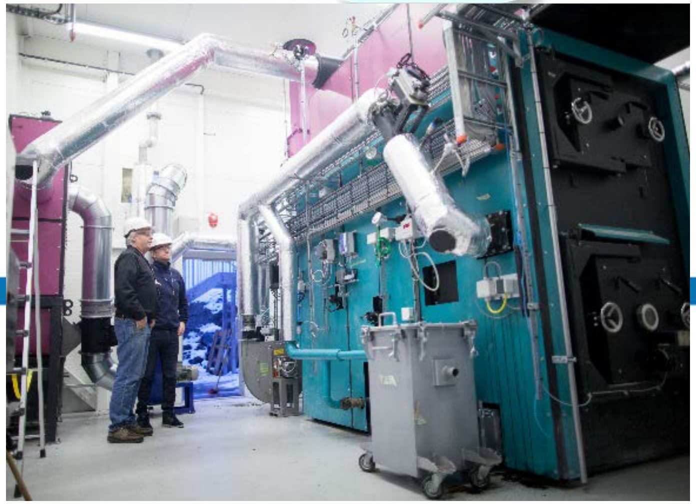
Multi-absorber concept example

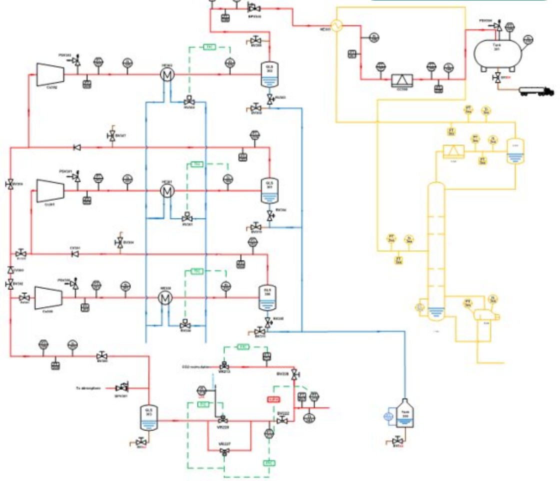
ATEX-proof mobile pilot fot testing onsite operating refinery



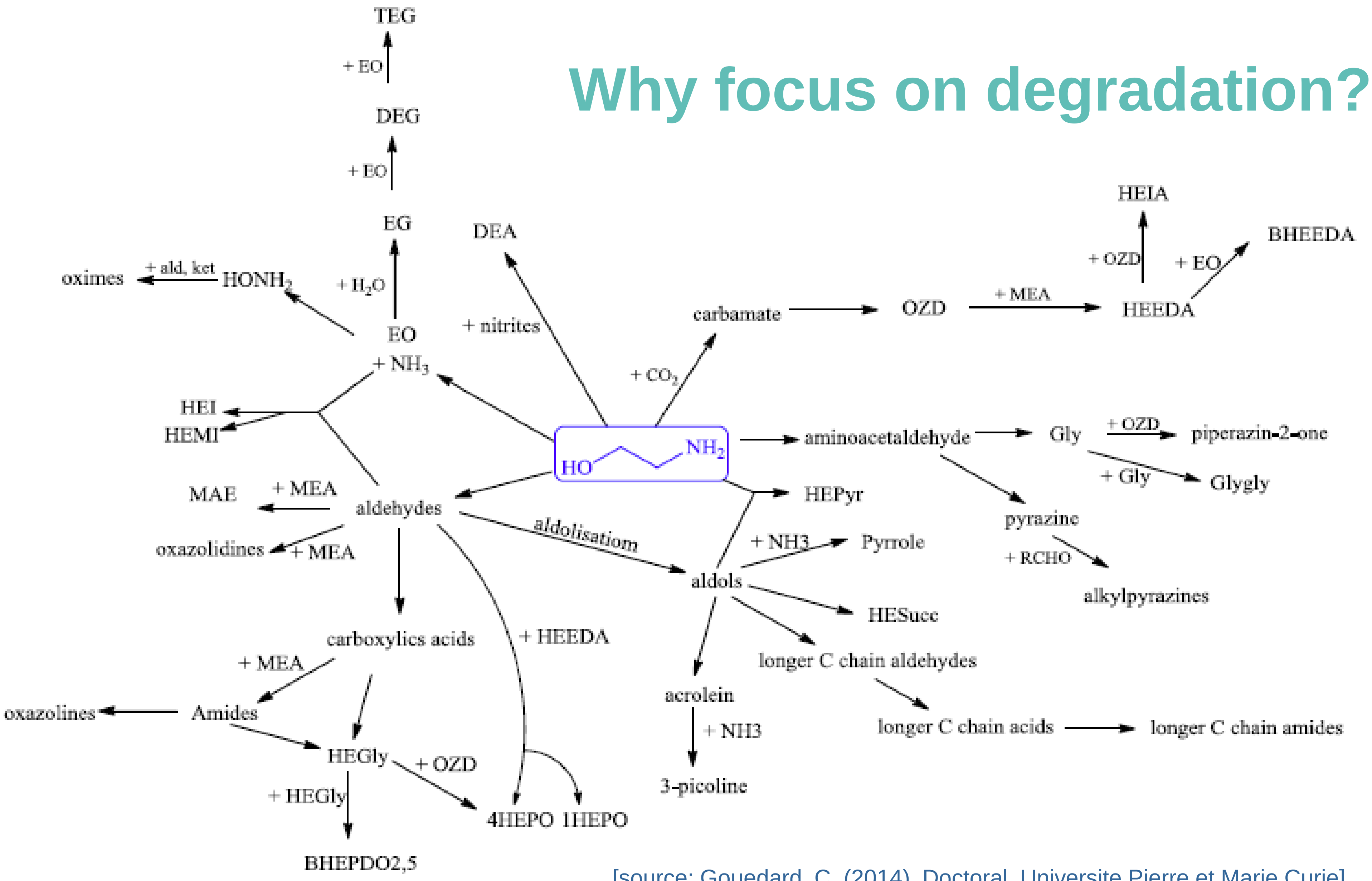
Full-height CO_2 capture pilot plant





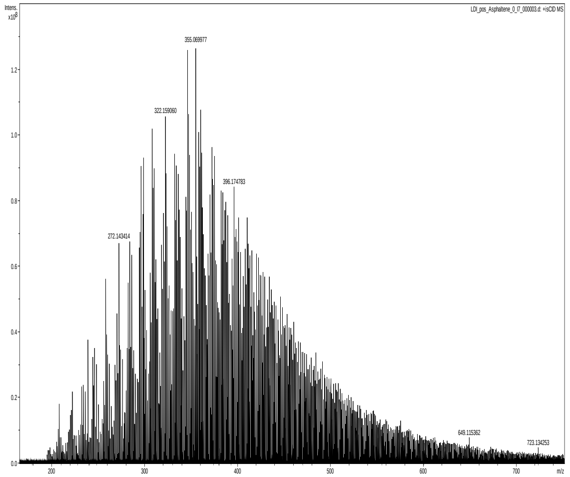


Why focus on degradation?



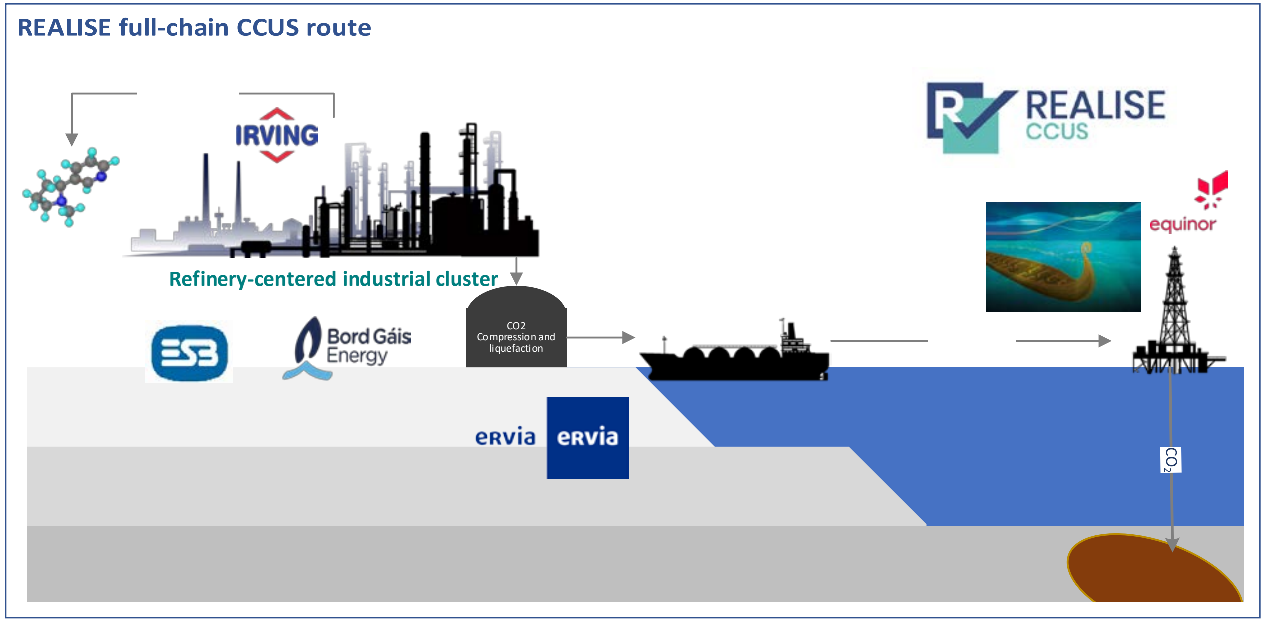
[source: Gouedard, C. (2014). Doctoral, Universite Pierre et Marie Curie]

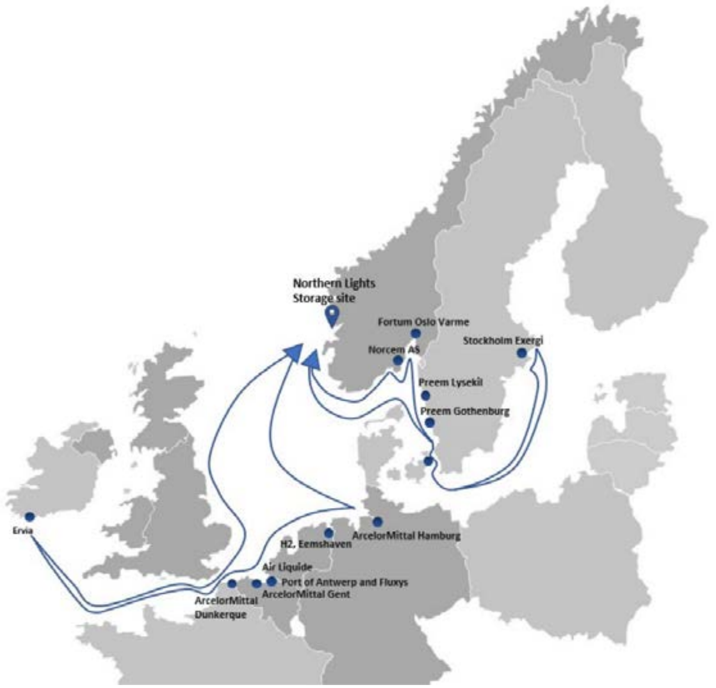
Advanced chemical analysis



Sampling of the cleaned gas from absorber (earlier project)

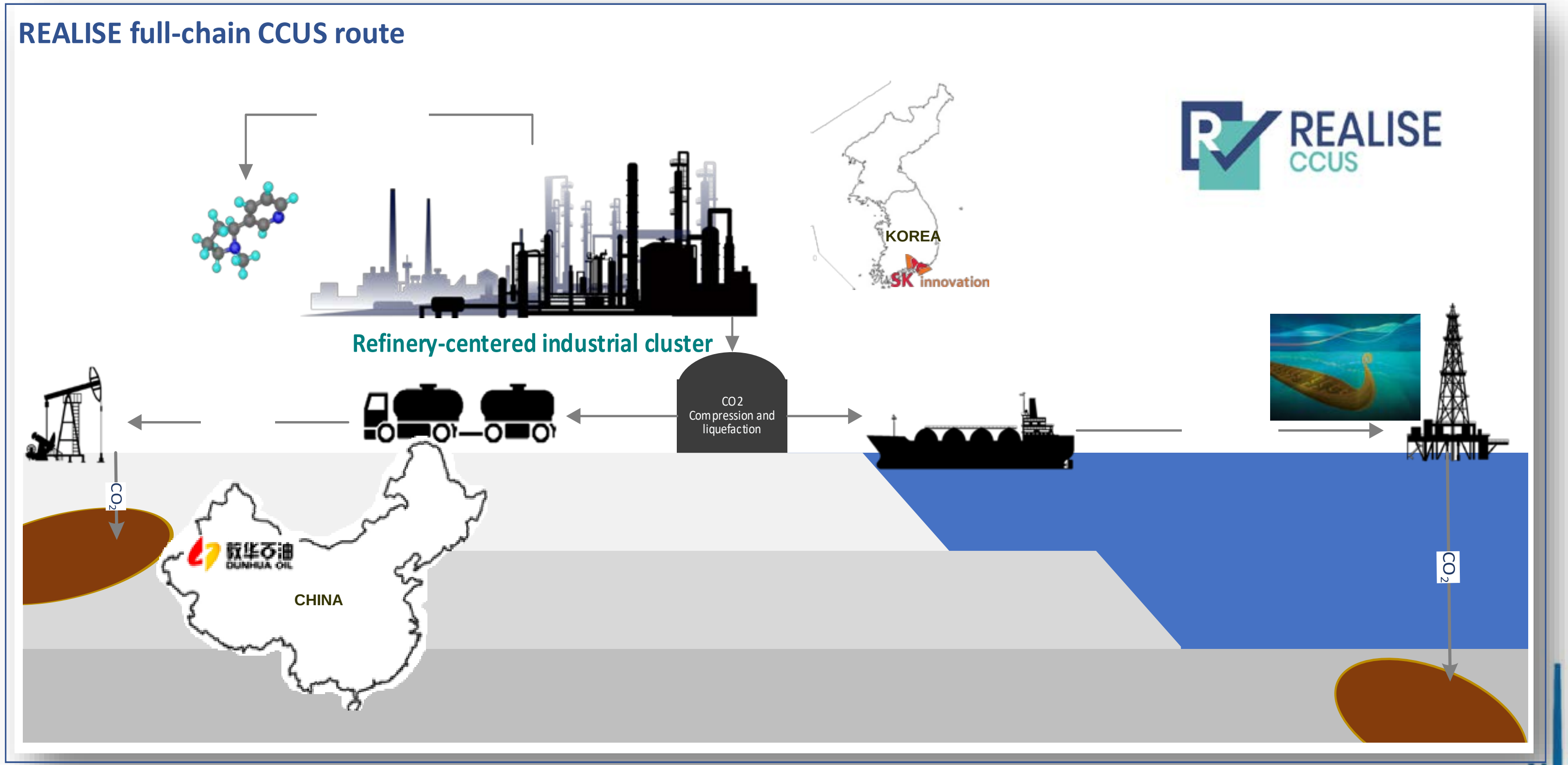
REALISE business cases: Ireland





Phase 1 of Northern Lights
(https://ccsnorway.com/wp-content/uploads/sites/6/2020/07/Plan-for-long-term-use-of-the-Northern-Lights-infrastructure-1.pdf)

Business cases in REALISE: China and South Korea



Stakeholders' engagement in REALISE

Industry Club

External experts **Advisory Board**

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884266

Thank you for listening

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Project

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C4U

International Workshop on CO_2 Capture and Utilization

Pilot preparation for demonstration in the C4U project

17 February 2021

Paul Cobden & Carlos Abanades

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 884418

C4U IS TYPICAL GOES ATYPICAL
C4U IS GOOD ATYPICAL

CaL
Calcium
Looping

SEWGS
Sorption-
Enhanced
Water
Gas Shift

C4U

Post-combustion Capture

Pre-combustion Capture

HIGH TRL MEANS UTILISING INDUSTRIAL SITES/GASES FOR DEMONSTRATION

Asturias

+17°C

CASOH

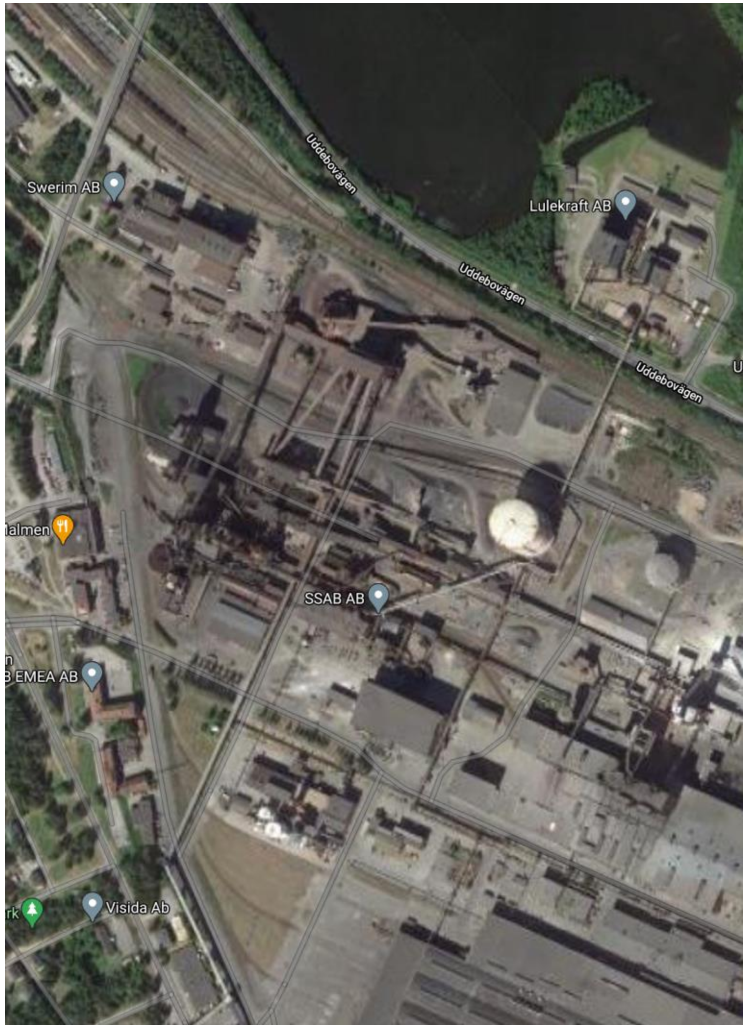
Ca-Cu

1°C/mm

Pre-combustion testing

4000 km

1°C/100km



Post-combustion testing

Luleå

-24°C

DISPLACE

Hydrotalcite

1°C/cm

STATUS OF PILOT PREPARATIONS

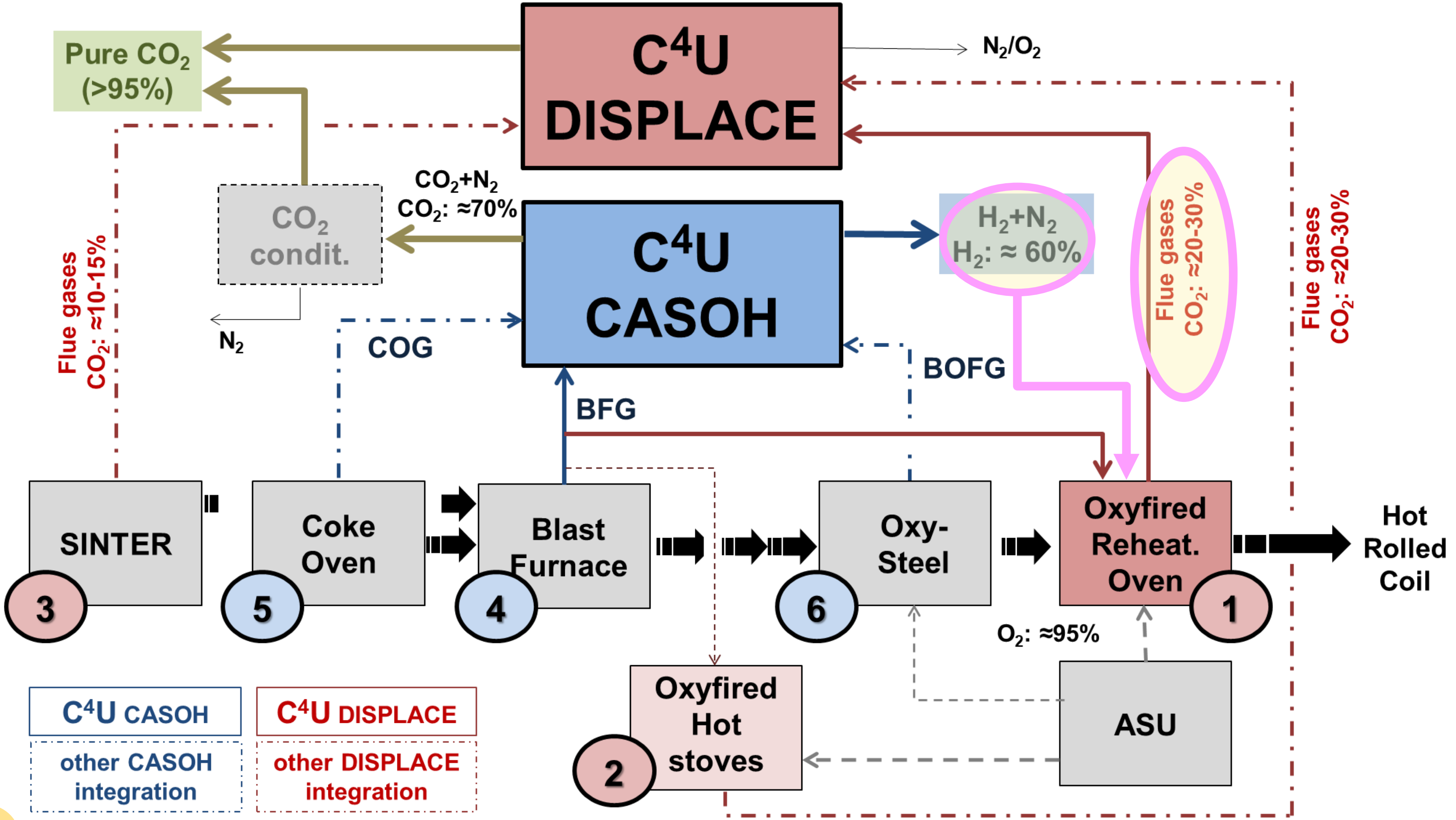
Similar Activities

- Both CASOH and DISPLACE will have 2000 hrs of demonstration at high TRL
- Most activities in 2020 and 2021 are engineering, procurement, construction
- DISPLACE has much of the equipment in place, and the linking of the unit is the main task
- CASOH requires a new pilot installation and building

Status

- Both CASOH and DISPLACE have achieved their respective deliverables on the basis of design
  - Special attention has been paid to the equipment delivery timeline
- Mass balances and operational philosophy of pilot
- All of the responsibilities of all of the involved partners in the different stages
  - Including delivery of the materials for testing, hydrotalcites, WGS catalysts, Ca-based sorbent and Cu-based materials
- Both CASOH and DISPLACE have delivered basic engineering and have started detailed engineering

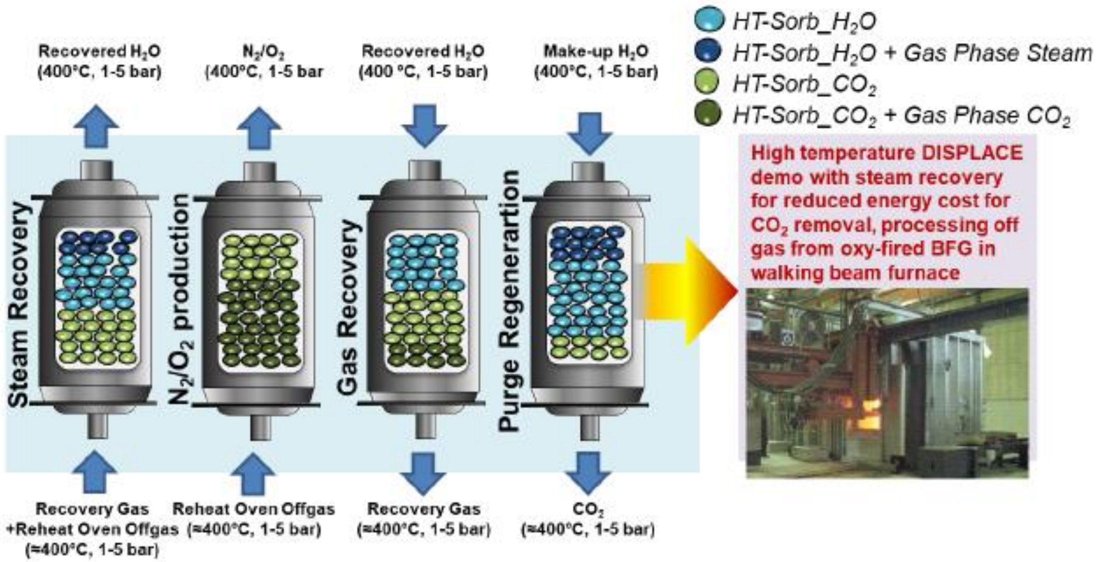
HOW DO TECHNOLOGIES FIT WITHIN C4U?

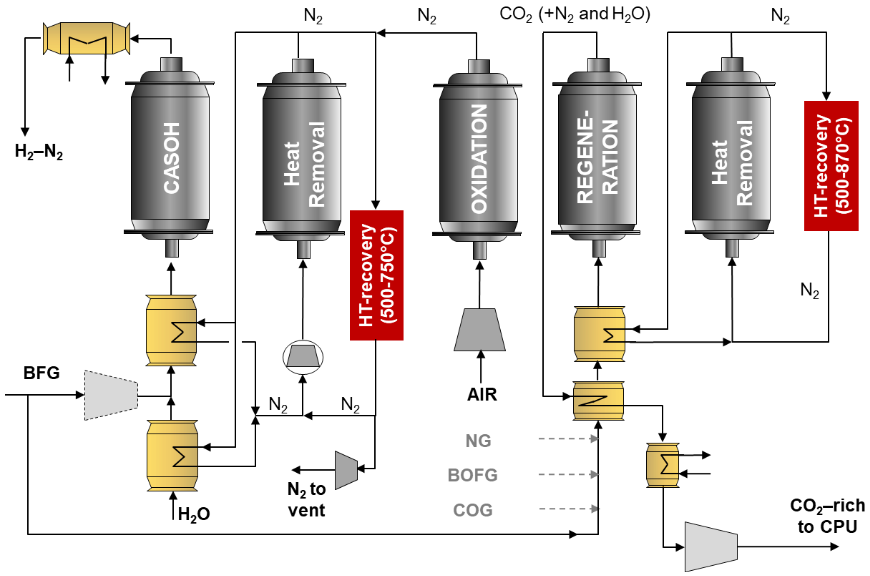


DEMONSTRATION OF CO_2 CAPTURE PROCESSES IN STEEL MILLS

DISPLACE design:
Define the optimal sizing, number and configurations of the DISPLACE process, so to reduce the capture costs and to minimize the steam use while attaining the CO_2 purity target in the real scale plant.

CASOH design:
Provide overall M&H balance,Provide the large scale reactor size, and dynamic operation modelling, Calculate the performance of the single process, Provide the final design based on the experimental campaign at TRL7





C4U

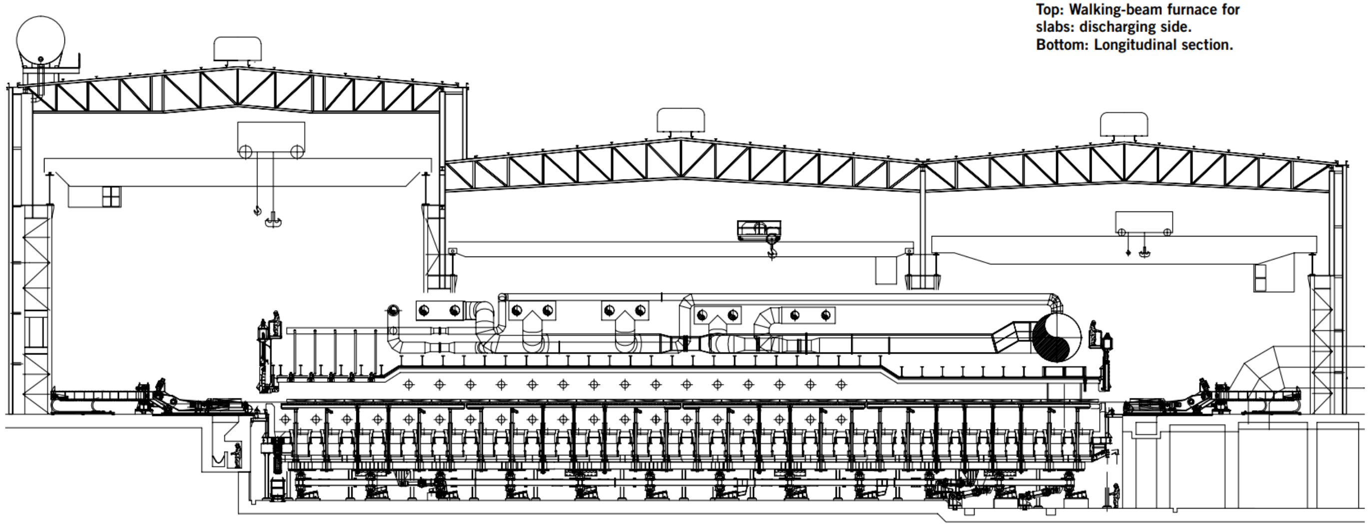
DISPLACE TECHNOLOGY OBJECTIVES

2 x 1000 hr campaigns

- N_2-H_2 Campaign, separation of H_2 from BFG, and subsequent H_2 use in chamber furnace
- DISPLACE Campaign, oxy-combustion of BFG in walking beam furnace, and CO_2 capture of oxy-combusted BFG

WHAT ARE REHEATING OVENS?

2.4 MT/y WBF



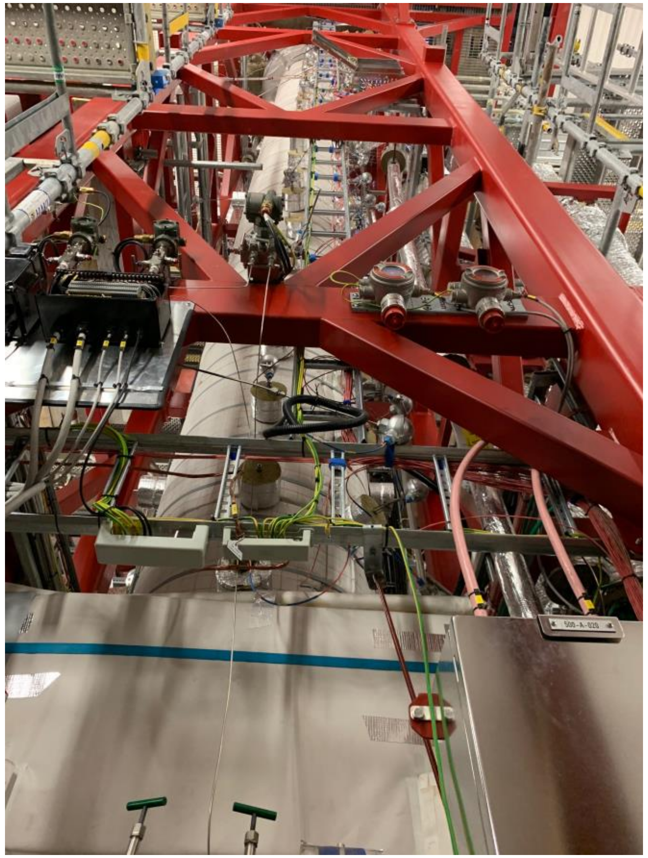
4

C4U

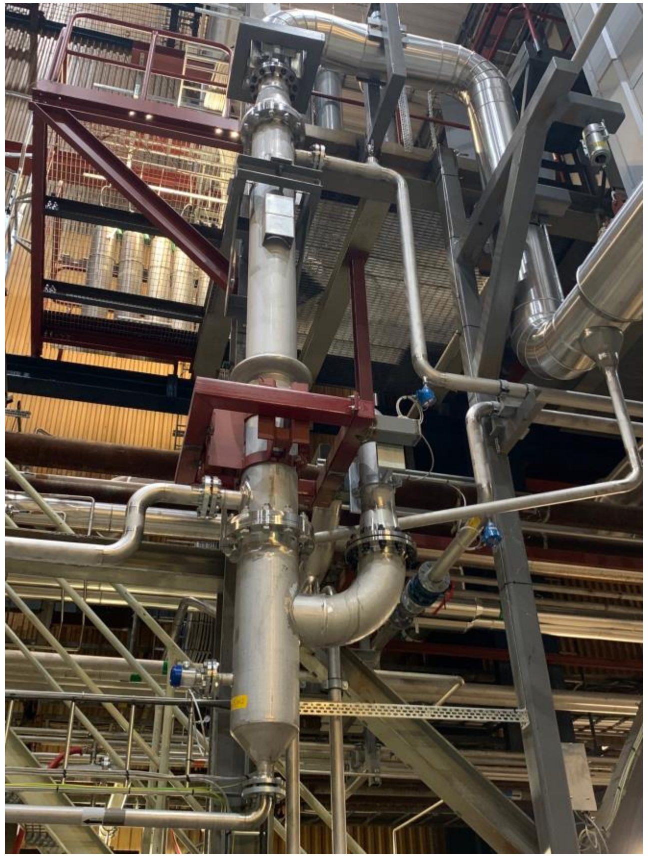
ArcelorMittal

DISPLACE: CO_2 CAPTURE EQUIPMENT

WGS (for N_2/H_2 campaign)



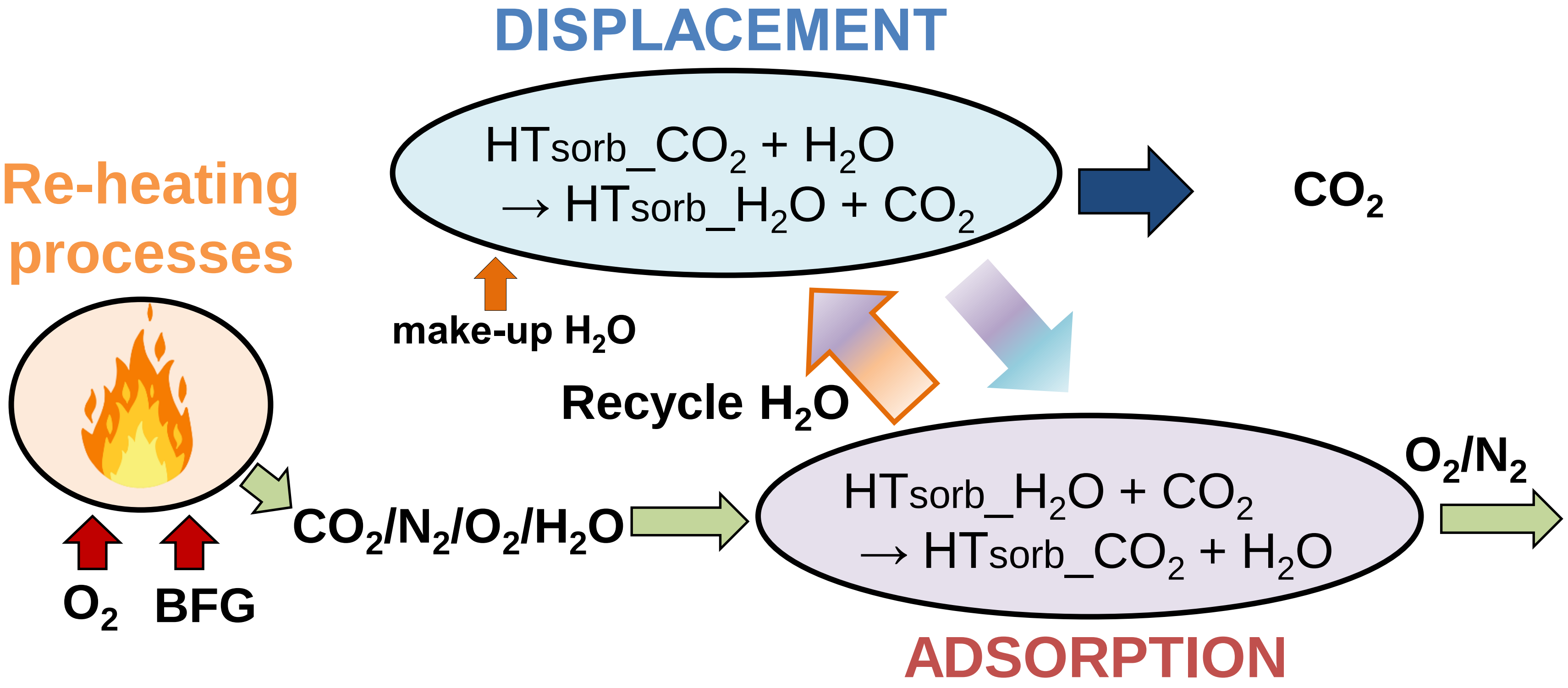
Single Column for N_2/H_2
Single Column DISPLACE



Syngas Cooler

C4U

DISPLACE PROCESS



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CASOH: Future location of the pilot at the AMA GasLab

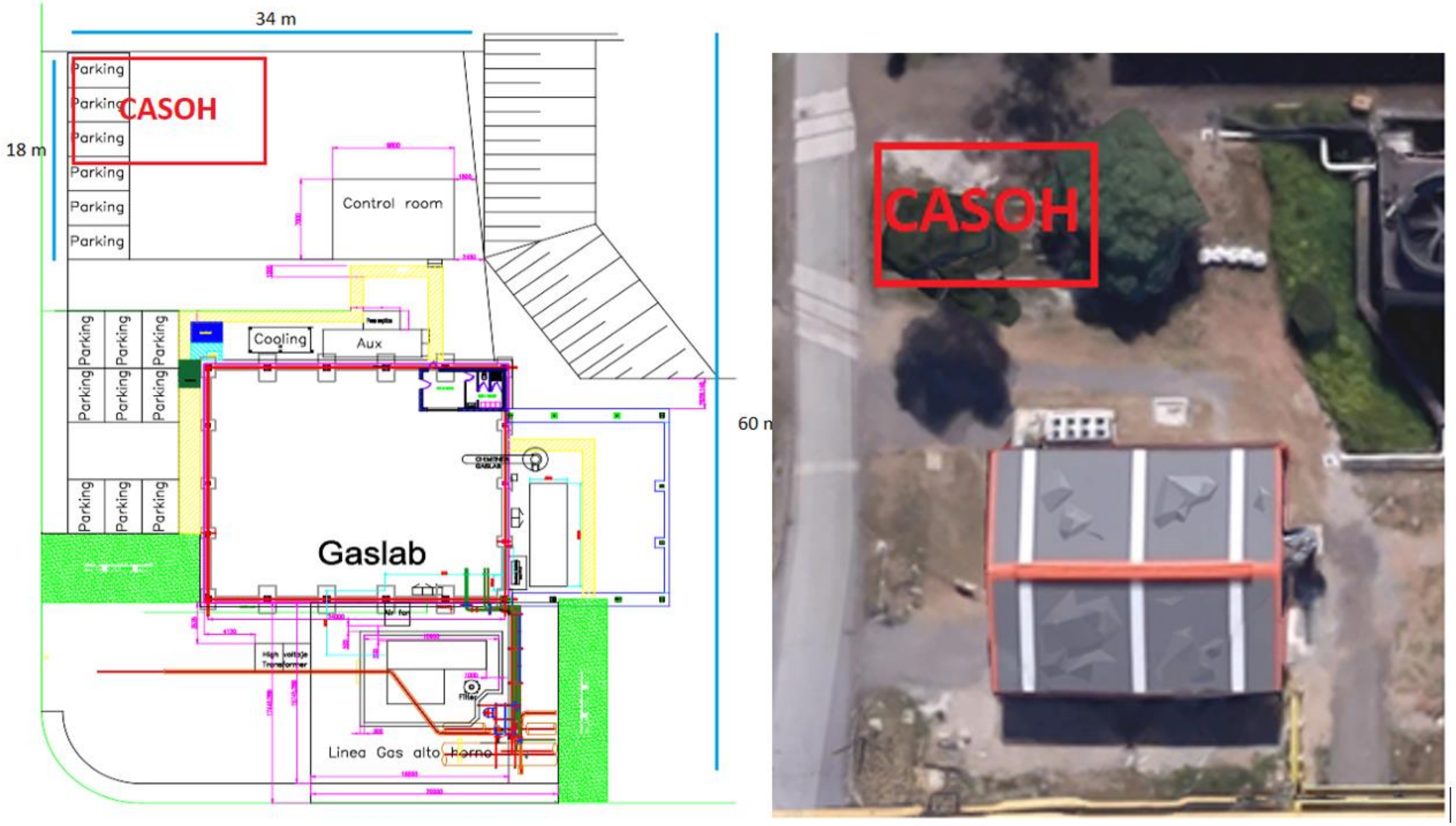
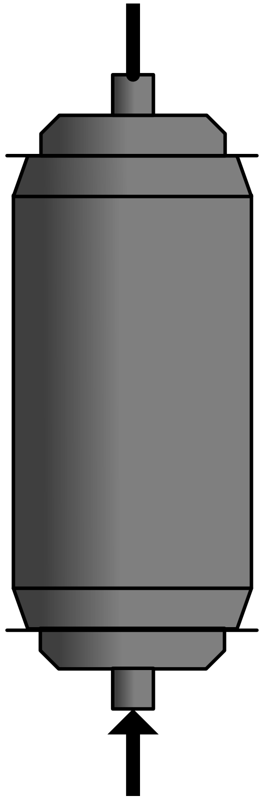


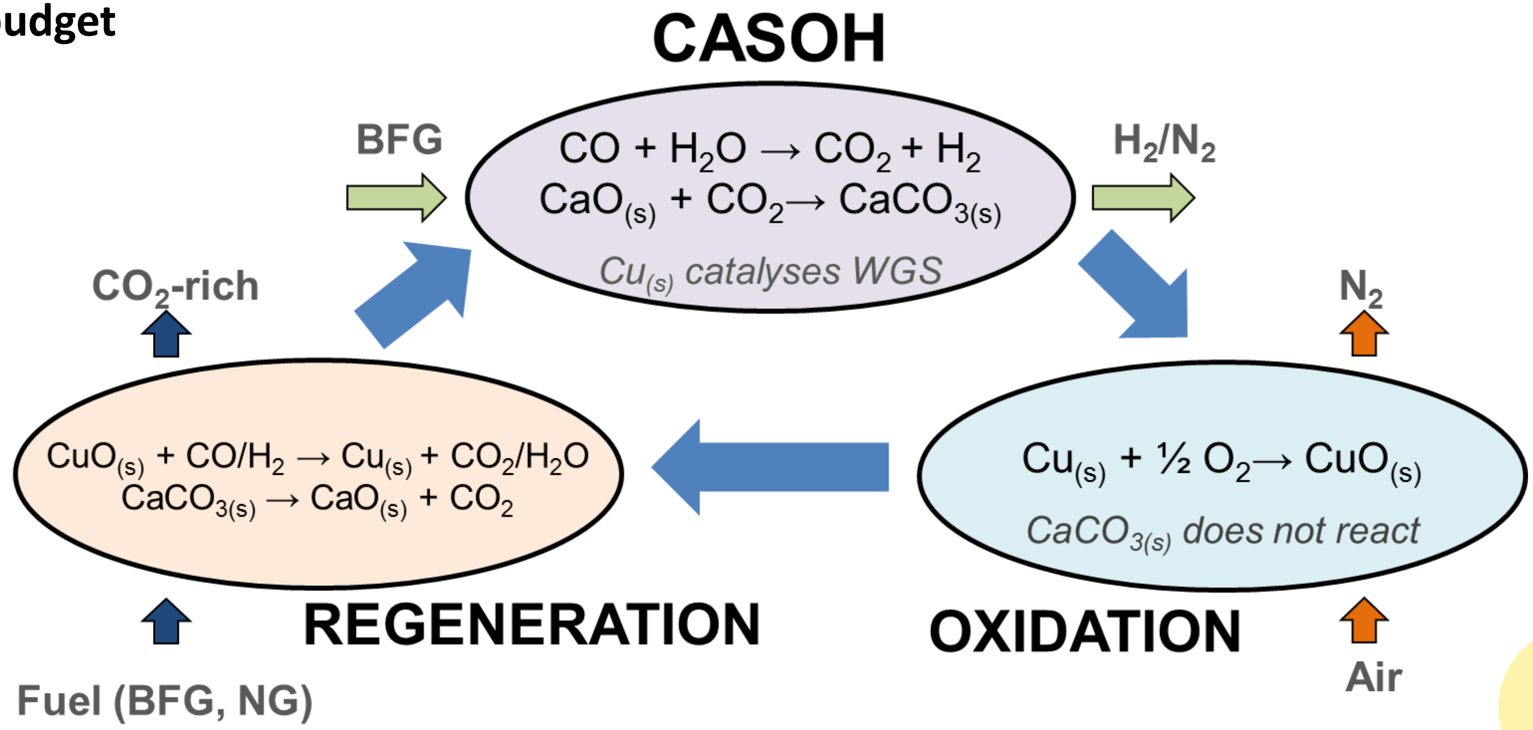
FIGURE 21. Pilot plant location next to Gaslab ArcelorMittal area.

CASOH REACTIONS FOR BLAST FURNACE GAS



Main drivers for pilot design

- A single packed bed reactor is the core of the pilot
- Demonstration of reaction stages is a priority (i.e.: vs the heat removal stages)
- High TRL scale (defined as 0.3 $MW_{LHVofH2}$ + 0.7 MW_{th} as HT heat from regeneration)
- Indicative dimensions: 5 m height, 0.5 m I.D.
- **Keep within budget**



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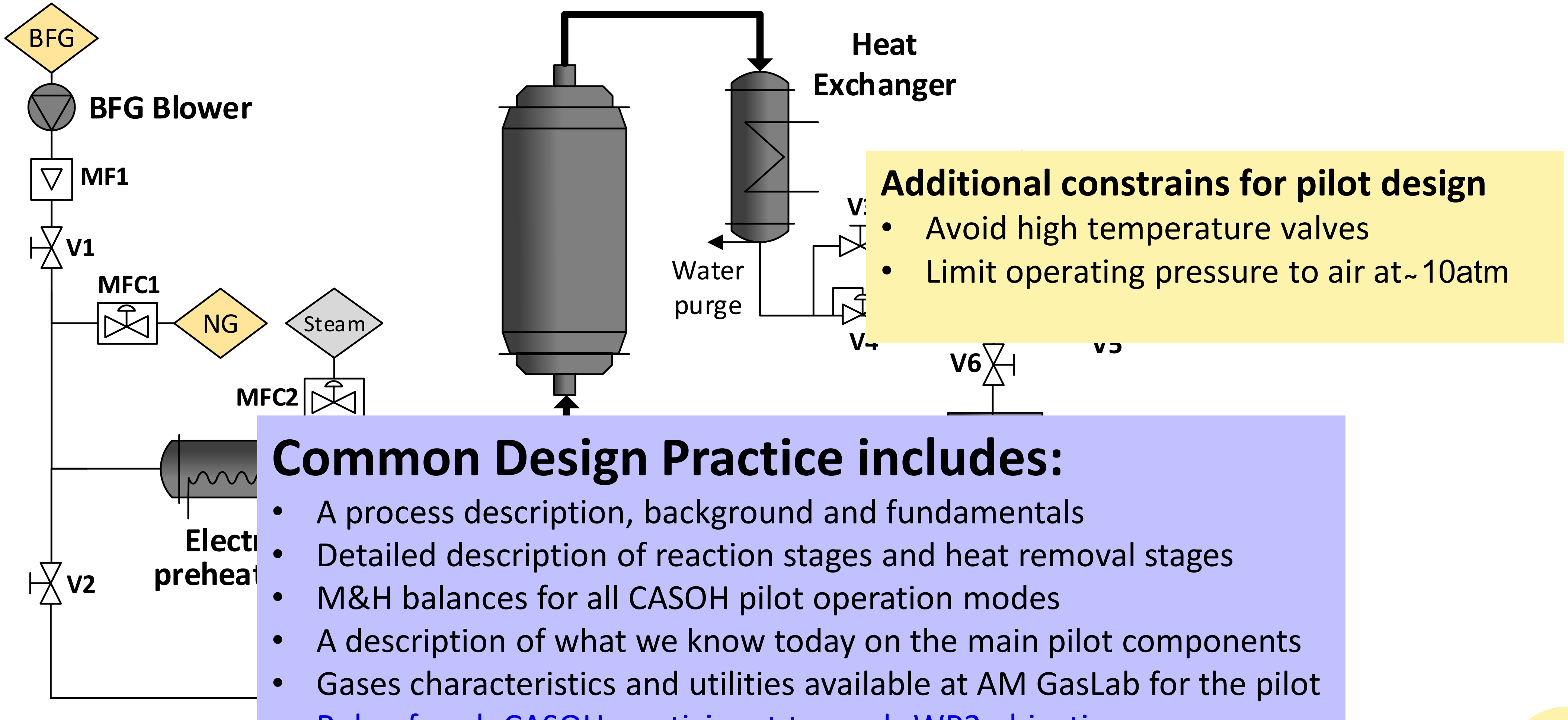
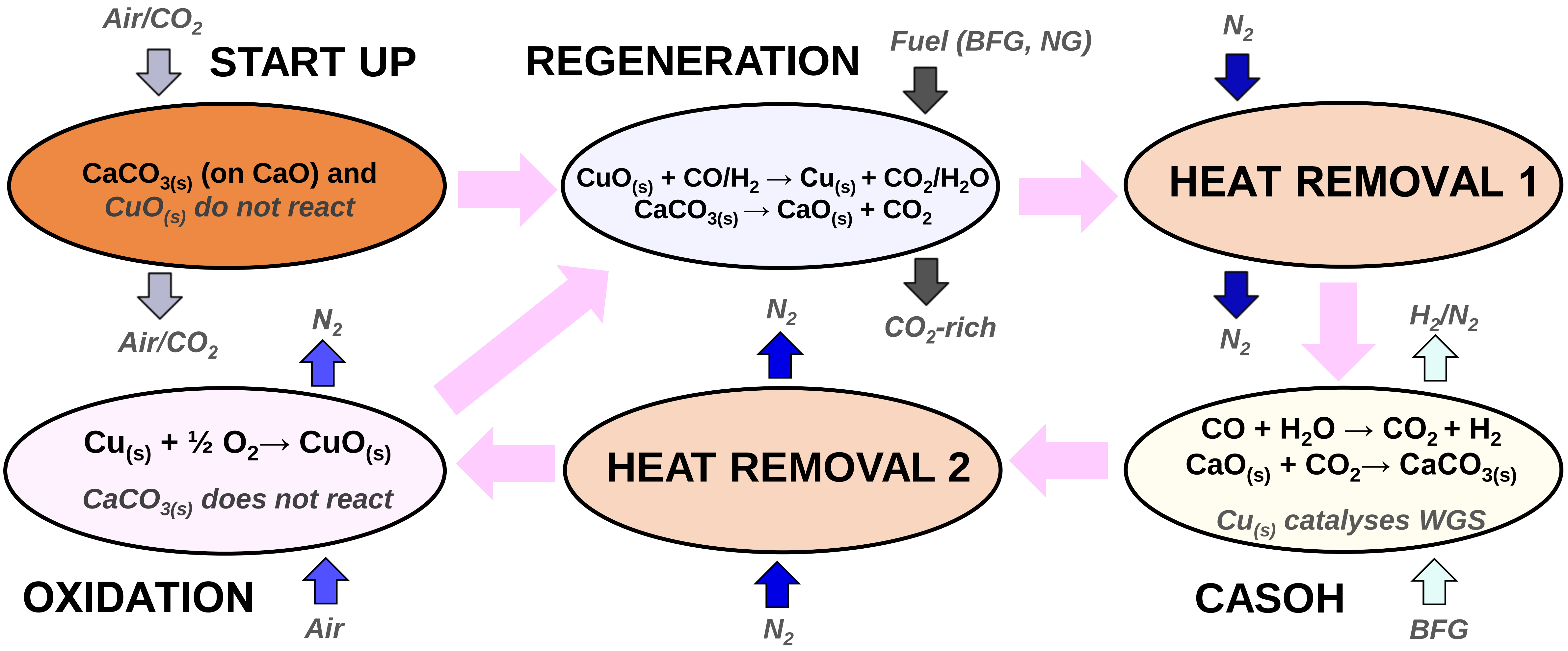
Process Flow Diagram of CASOH pilot



Additional constrains for pilot design
- Avoid high temperature valves
- Limit operating pressure to air at~10atm

Common Design Practice includes:
- A process description, background and fundamentals
- Detailed description of reaction stages and heat removal stages
- M&H balances for all CASOH pilot operation modes
- A description of what we know today on the main pilot components
- Gases characteristics and utilities available at AM GasLab for the pilot
- Role of each CASOH participant towards WP2 objectives

FULL OPERATION SEQUENCE IN THE PILOT

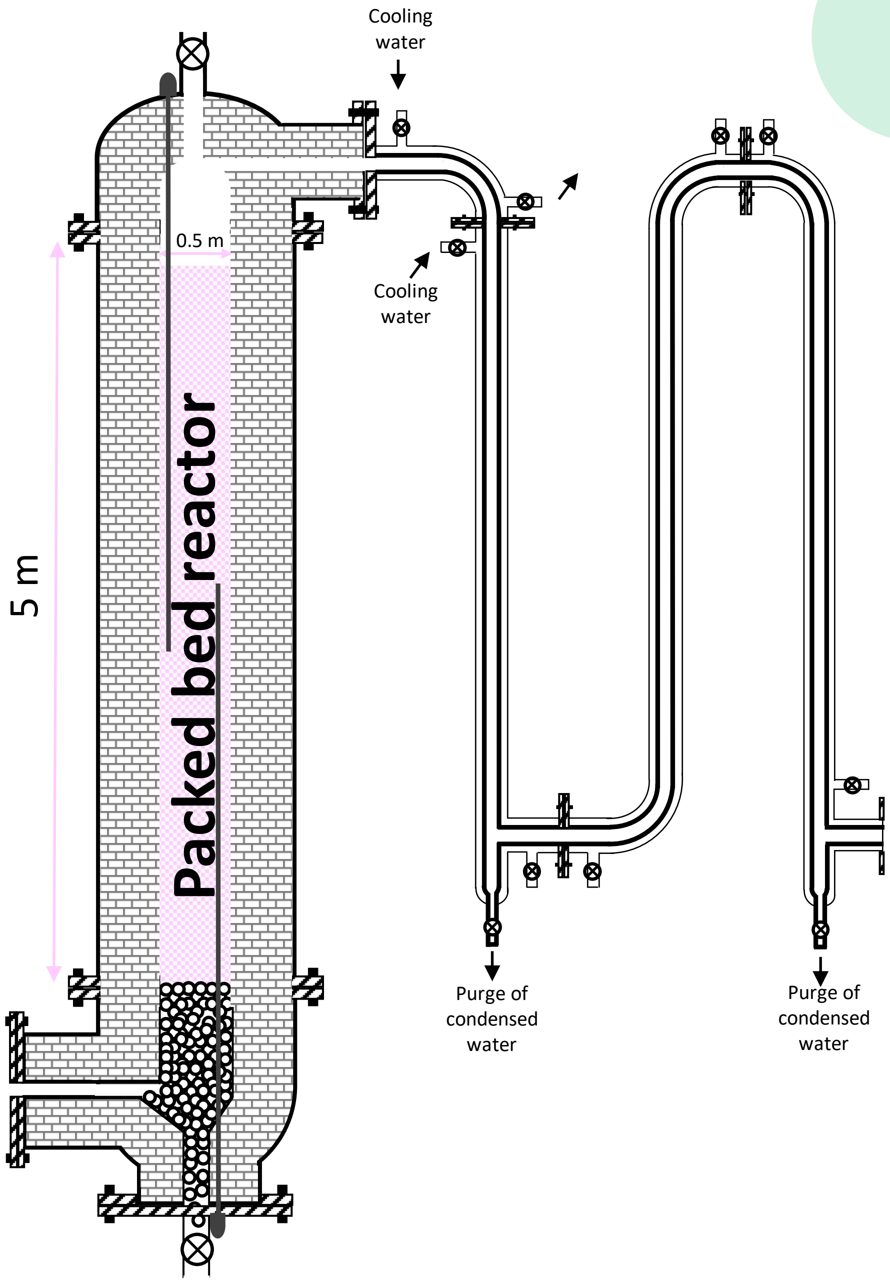


DESIGN STATUS OF MAIN PILOT COMPONENTS

Bed characteristics	
CaO active, %w	10
Cu active, %w	30
Particle size,mm	3

Reactor characteristics	
Height, m	5
Diameter, m	0.5
Cu/Ca molar	1.8
Mass Ca-, kg	900
Mass Cu-,kg	600
Total bed mass, kg	1500

Samples of candidate materials from Carmeuse and Johnson Matthey received for lab. testing



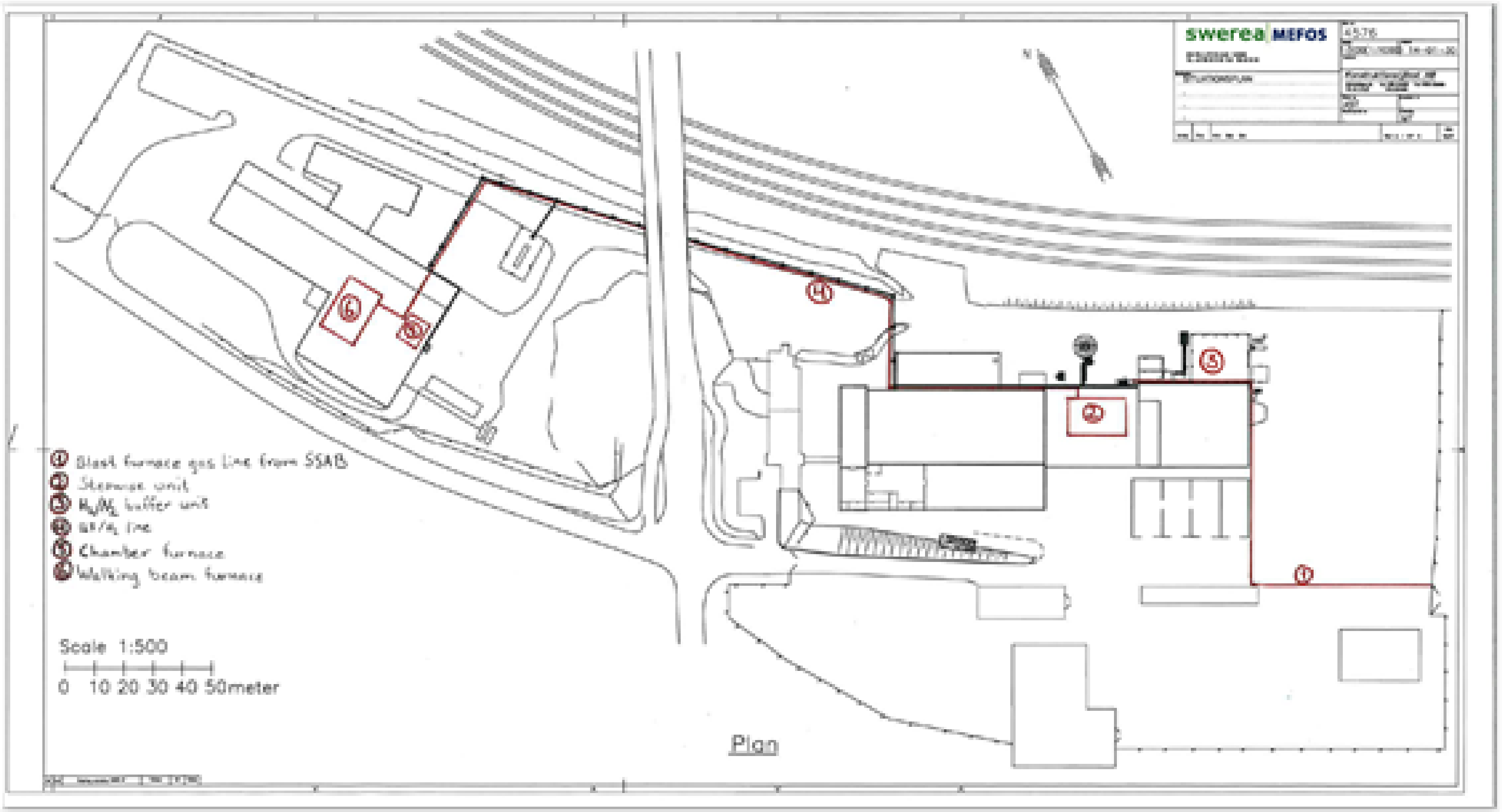
DISPLACE CDP & BOD : COMMON DESIGN PRACTICE AND BASIS OF DESIGN

CDP

- Describes all partners activities and responsibilities for all partners involved in building and operating the pilot plant
- i.e. a more detailed description of scope compared to the DoA

BOD

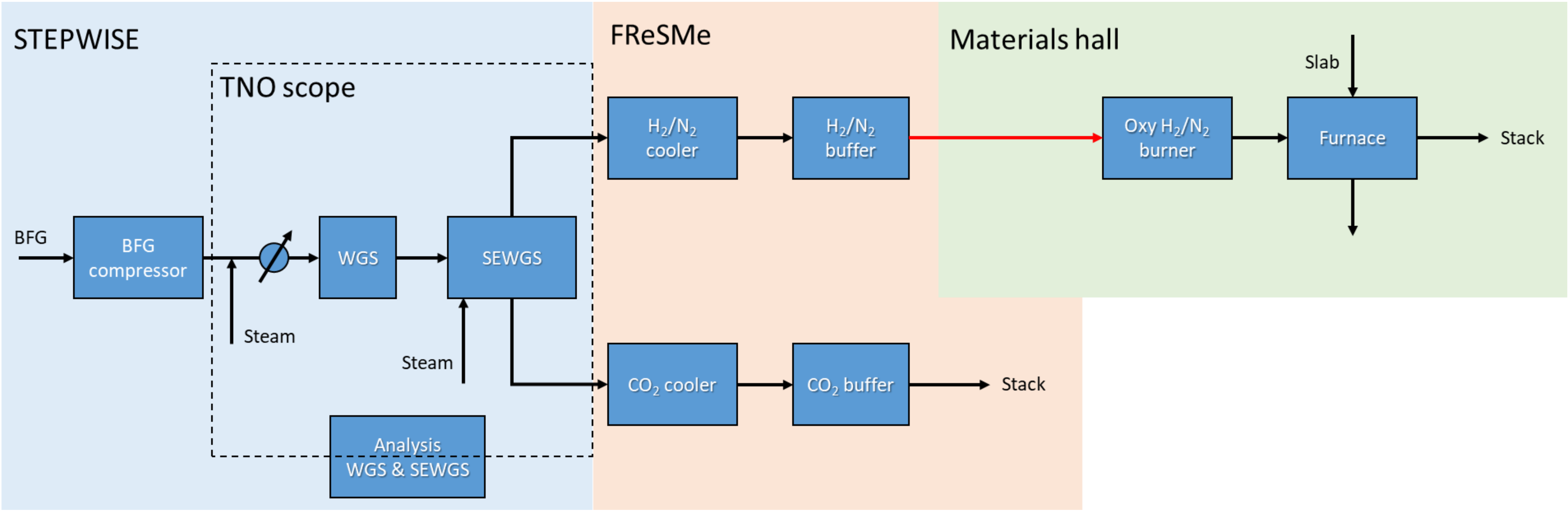
- Initial layout of equipment (see right)
- Mass and Energy flows and balances to drive basic engineering phase



C4U

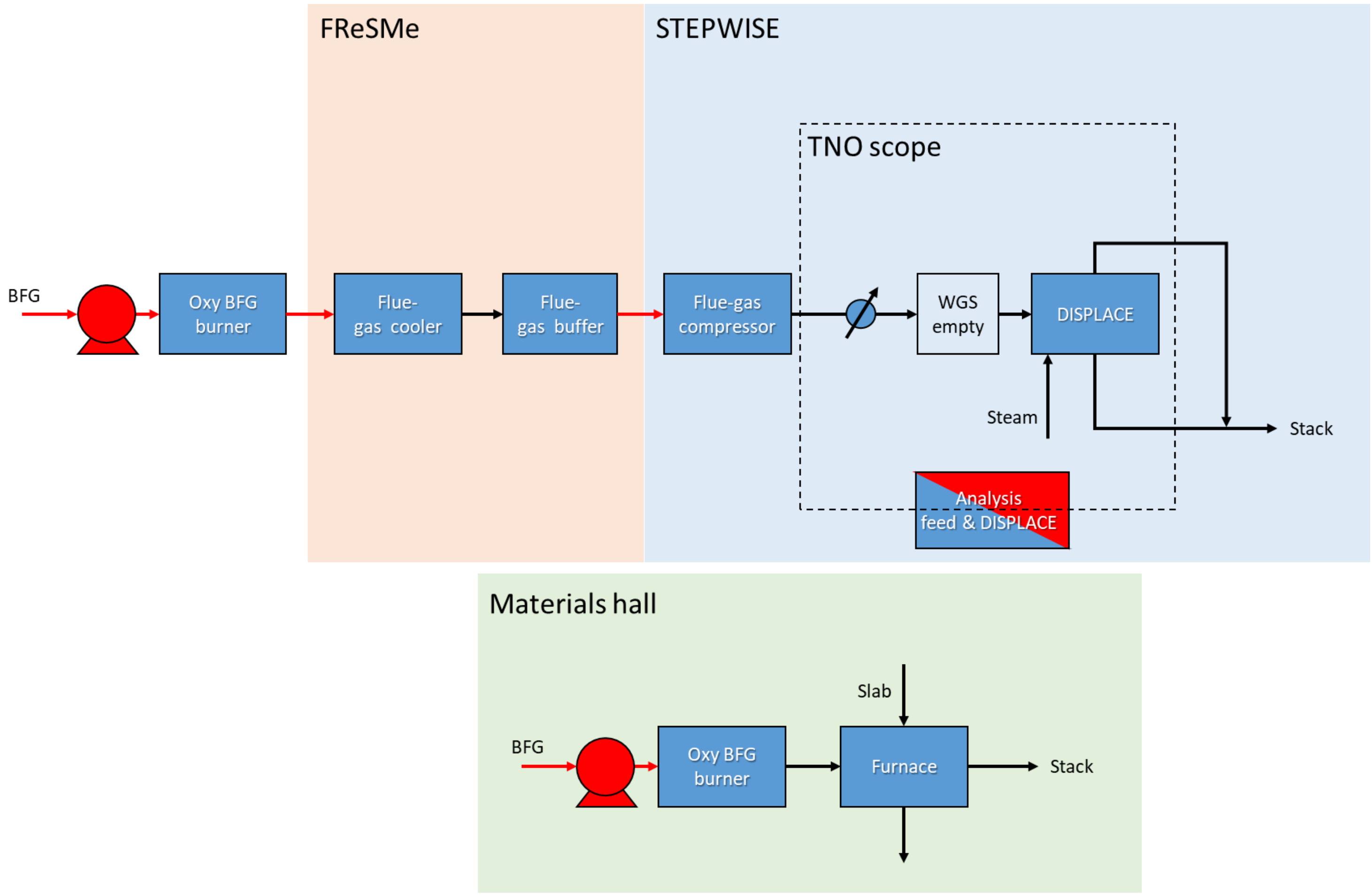
CONFIDENTIAL

CPD & BOD N_2/H_2-CAMPAIGN



Campaign 1 : N_2/H_2 – SEWGS Campaign

CPD & BOD – DISPLACE CAMPAIGN



Campaign 2 : Oxy-BFG – DISPLACE Campaign

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SYNERGIES BETWEEN CASOH AND DISPLACE

CASOH

Coke Oven Gas

Basic Oxygen Furnace Gas

Blast Furnace Gas

N_2-H_2 product as fuel

DISPLACE

Sinter Plant Exhaust

Hot stoves

Reheating Furnaces

Blast Furnace Gas processed by CASOH

C^4U

C4U

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DENS CCS

Formic acid as a liquid
organic hydrogen carrier

About DENS

invented in
2015

Founded in
2018

Employees
24

Homebase
HELMOND

'Pico" the first proof of priniciple 2.5W

2015

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

The first 25W prototype

2016

TEAM FAST

Hydrozine range extender concept for a bus

2017

TEAM FAST

First practical test with system construction site

2018

TEAM FAST

DENS' X1 2kW power equipment

2019

DENS

DENS' X2 20kW Stroom generator First field pilots

2020

Start of serie production

2021

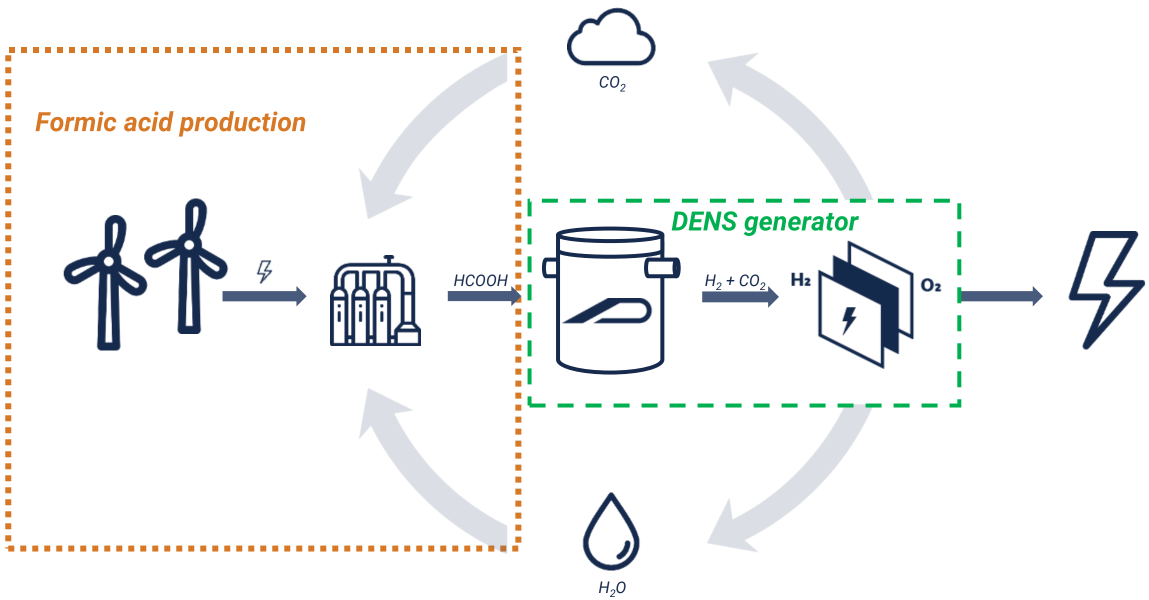
DENS

heijmans

TBI infra

F&L POWERRENTAL

CO2 neutral energy carrier

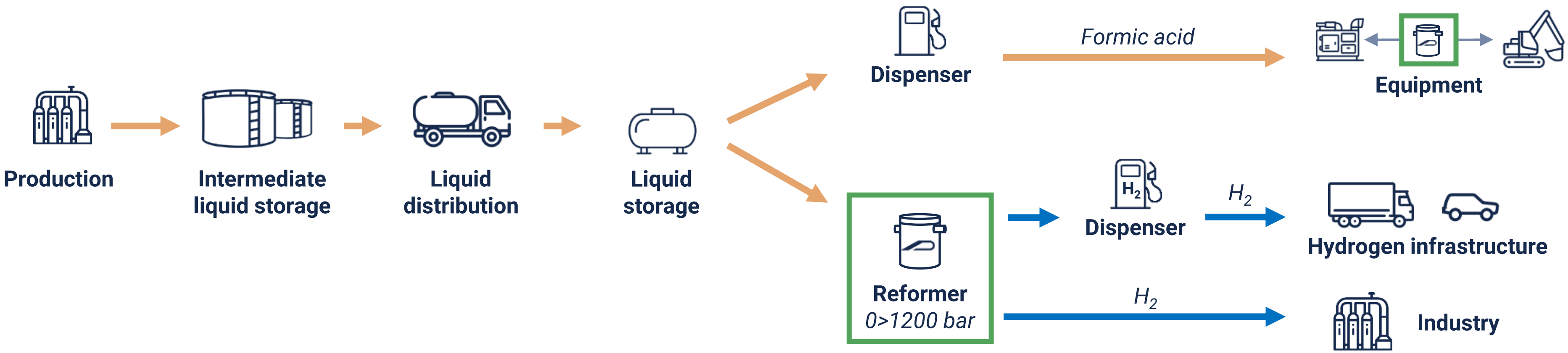


Formic acid reconversion value proposition

By using DENS' reformer technology, hydrogen's storage and transport issues can be easily overcome.

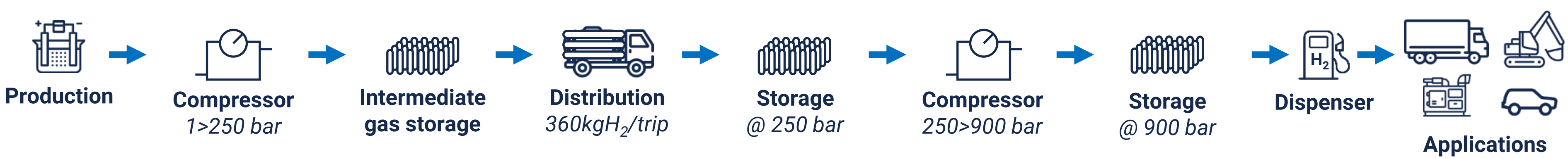
The hydrogen economy with DENS

Storage and transport of formic acid, is significantly cheaper and safer, and therefore accelerates the hydrogen economy. DENS can convert formic acid back into hydrogen for direct use in a fuel cell or to allow for hydrogen generation on demand from liquid storage.



Current hydrogen economy

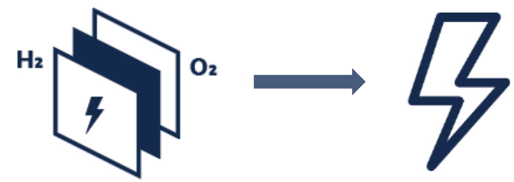
Storage and transport of gaseous hydrogen is highly expensive and therefore limiting the adoption of the hydrogen economy.



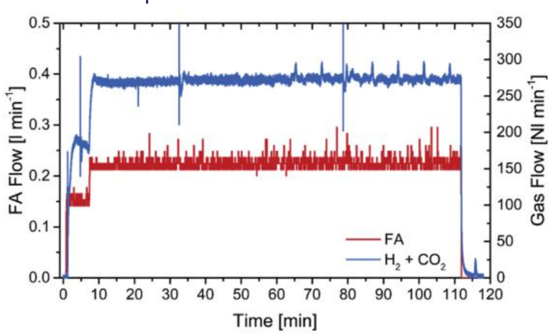
DENS generator technology

Reformer technology

Fuel cell technology



- ✓ Instantaneous reaction at low temperature



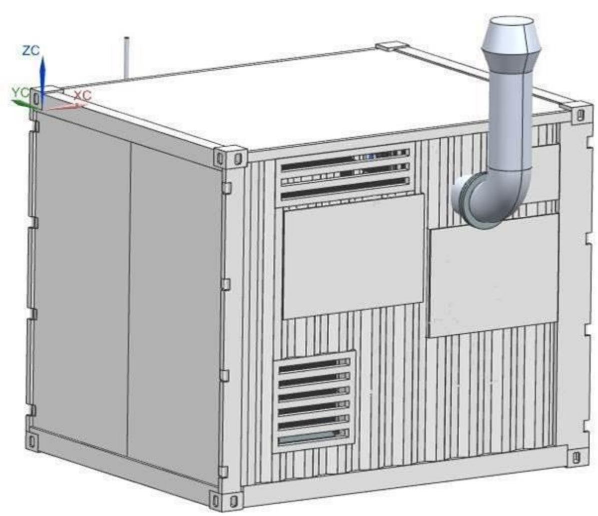
- ✓ Very little impurities
- ✓ Works up to 1200 bar

- ✓ Low temperature PEM
- ✓ Broadly certified stack
- ✓ Mass produced by BOSCH

Results

First field tests are being preformed

- Gas quality stays good to keep using the fuel cell also outdoors
    - CO production well below given target of fuel cell
    - FA levels are also well below given target value of fuel cell
- Stable reformer production for over 1000 hours
- 10 kw of nominal power achieved for at least 200 hours
- System optimalisations are being performed
- New insights in lifetime optimilisation are being tested
- Start and shutdown behaviour is being investigated



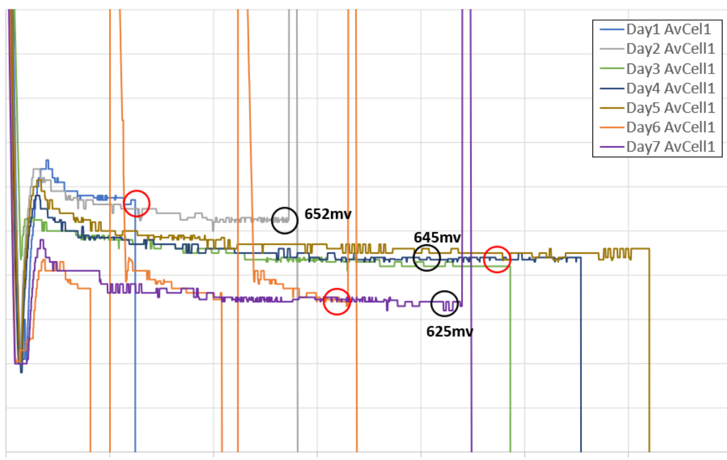
Results

Electrical components

- System has converted all the power to the local grid, enough for 20 households during tests
- Safety components have been checked by Lloyds and CE marking was checked
- Subsystem was tested and was capable of handling 30 kw's of power

Degradation

- Some degradation is witnessed not during runs but inbetween and not always
- Different Shut down and start procedures are being investigated together with partners, possible solutions are being tested (mainly due to emergency stops)



Planning

Tests are going to be performed at the end of the project at dk6 in Dunkirk

- Safety documents are being completed together with Engie
- Prelimary tests are being performed to solve start stop degradation
- Reformer components are being evaluated to make sure all wear and tear is being recorded and noted

Formic acid versus hydrogen

Hydrogens adoption barriers can be overcome via the liquid organic hydrogen carrier (LOHC) **Formic acid** in combination with **DENS' reformer**.

Adoption barriers

1. Pressurized gas storage
   - × Compressed at 200-700 bar.
   - × Liquified at -253 °C.
   - × Elevated safety risks.
   - × Expensive compression cost.
2. Gaseous distribution
   - × Expensive tube trailers.
   - × Only 360kg H_2 per trip.
3. Compression required
   - × Mechanical compression is required for refueling.
   - × Expensive compression cost.

vs.

Barrier breakers

1. Liquid storage
   - ✓ Ambient pressure.
   - ✓ Limited to no safety risks.
   - ✓ Affordable liquid pumping.
2. Liquid distribution
   - ✓ Affordable liquid trailers.
   - ✓ 4x more per trip (1431kg H_2).
3. Hydrogen production on demand
   - ✓ Chemical compression up to 1200 bar.
   - ✓ No additional energy required.
   - ✓ 100% renewable.

Expensive hydrogen H_2 **Affordable hydrogen**

Max Aerts | CEO

+31620276608 | max.aerts@dens.one

Design and development of a membrane based post-combustion CO_2 capture system

Workshop on CCUS
16-17 / 02 / 2021
www.iwccu.org

Leonardo Roses

Contact: *leonardo.roses@hygear.com*
www.hygear.com

Outline

- Introduction to HyGear
- Introduction on CO_2 emissions
- Processes for CO_2 Capture
- MEMBER objectives
- Design requirements for demonstration at industrial site
- Design and development of post-combustion CO_2 capture system
- Conclusions and final remarks

FACTS AND FIGURES

Established in 2002

With the mission to develop cost-effective gas supply

82

Highly motivated employees with an entrepreneurial and innovative spirit

> €23m

Gross revenue

66

Installations operational worldwide

14

patents securing a sustainable competitive edge

Industries that we are active in

Flat/float glass manufacturing
Metal sintering
Food
Electronics
Semiconductor
Fuelling station for vehicles

> 85,000 kg

CO_2 reduction per customer per year with breakthrough technologies

Active in

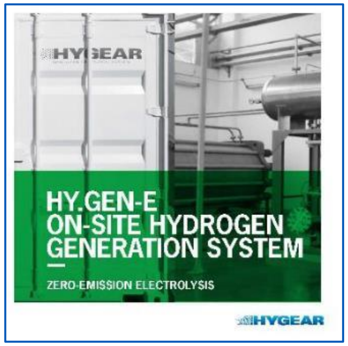
20 countries

PRODUCTS & SERVICES

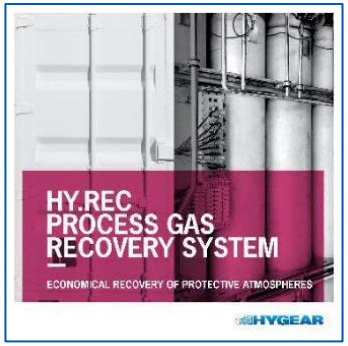
DELIVERING GASES THROUGH ON-SITE TECHNOLOGY

Hydrogen
Cost-effective
Steam Methane Reforming

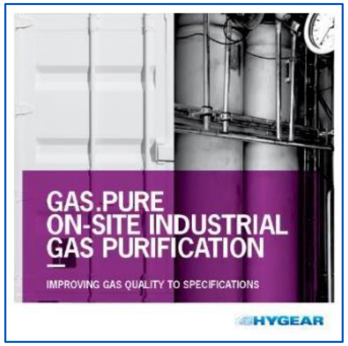
Hydrogen
Electrolysis



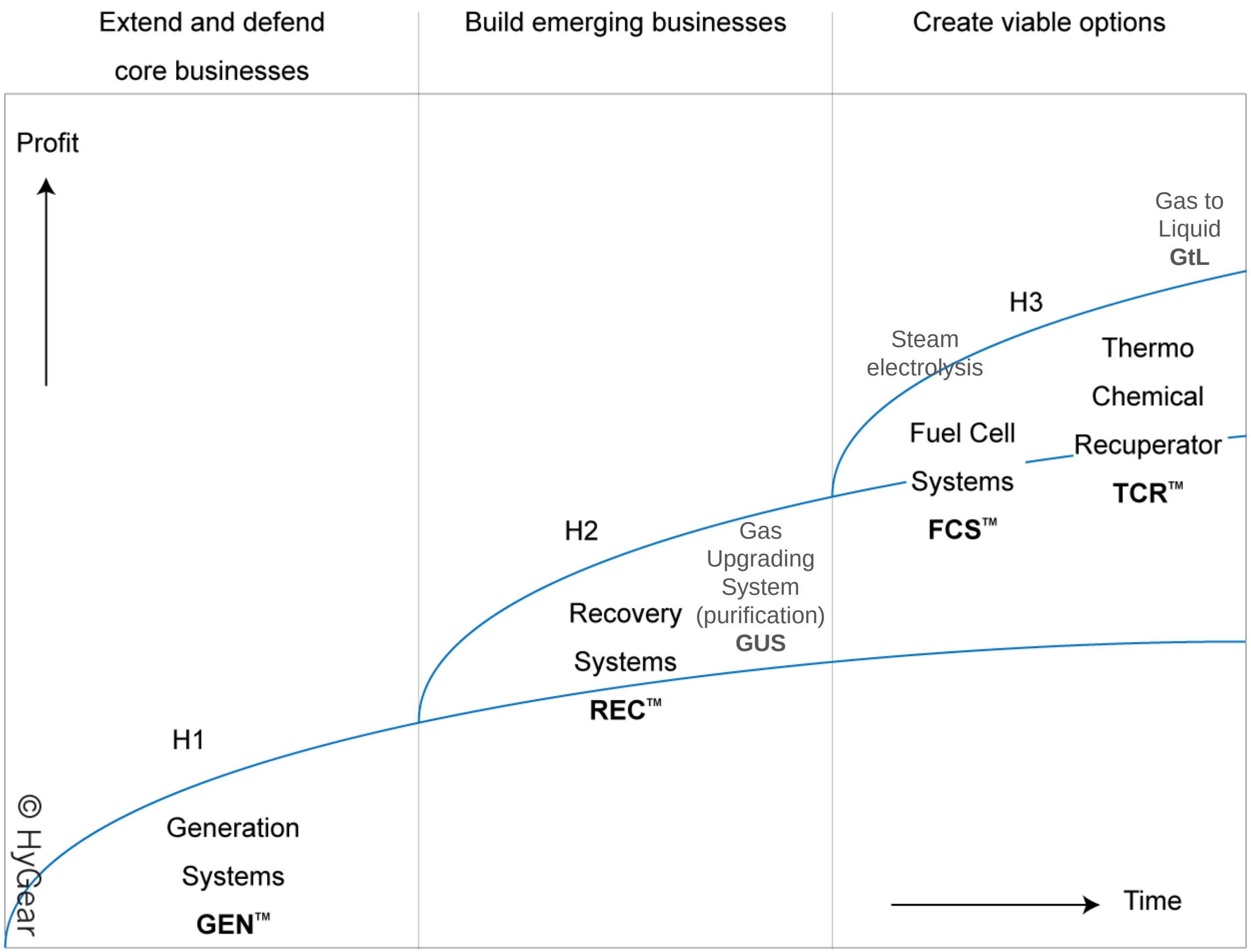
Gas Recycling
Economical recovery of gases
used as protective atmospheres



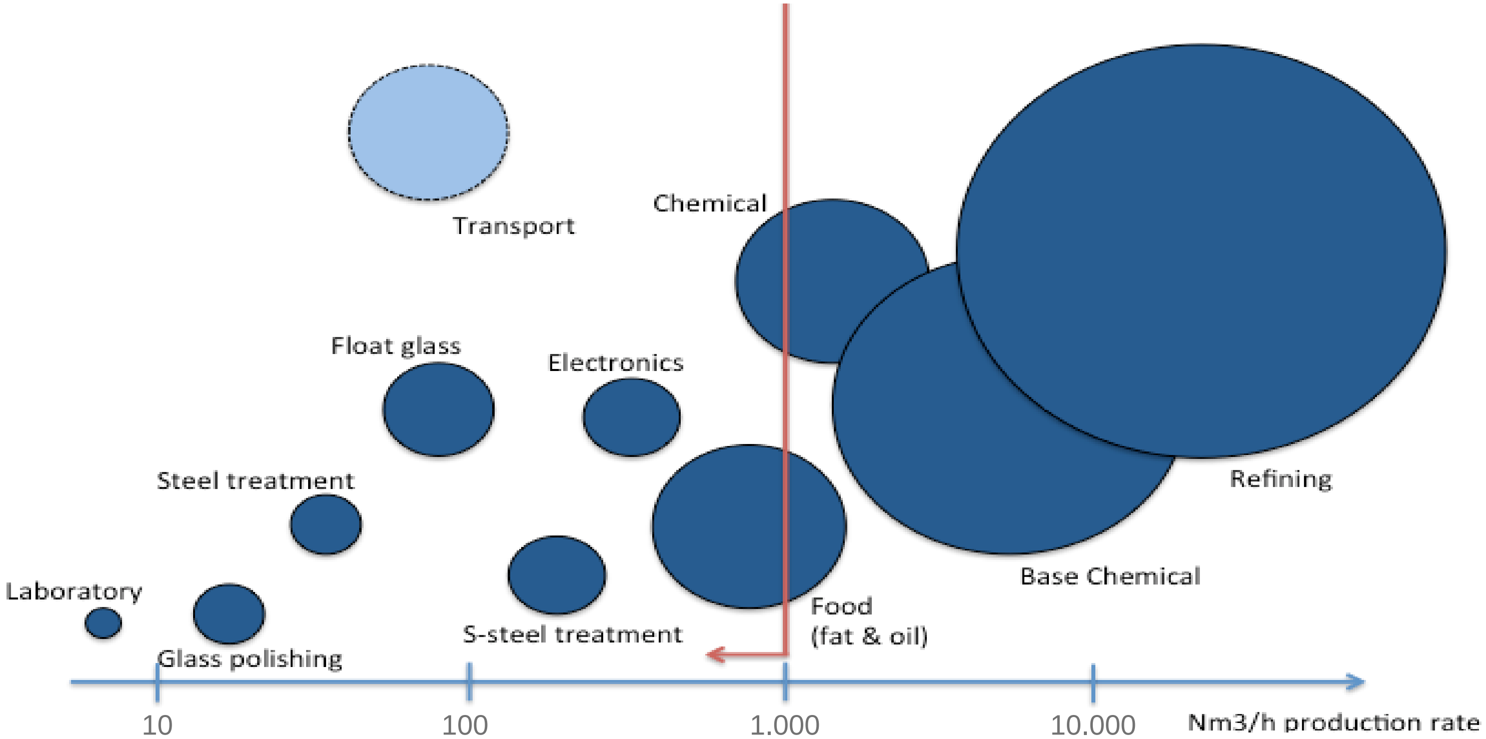
On-site Purification
Improving gas quality to
application required specifications



DEVELOPMENT STRATEGY

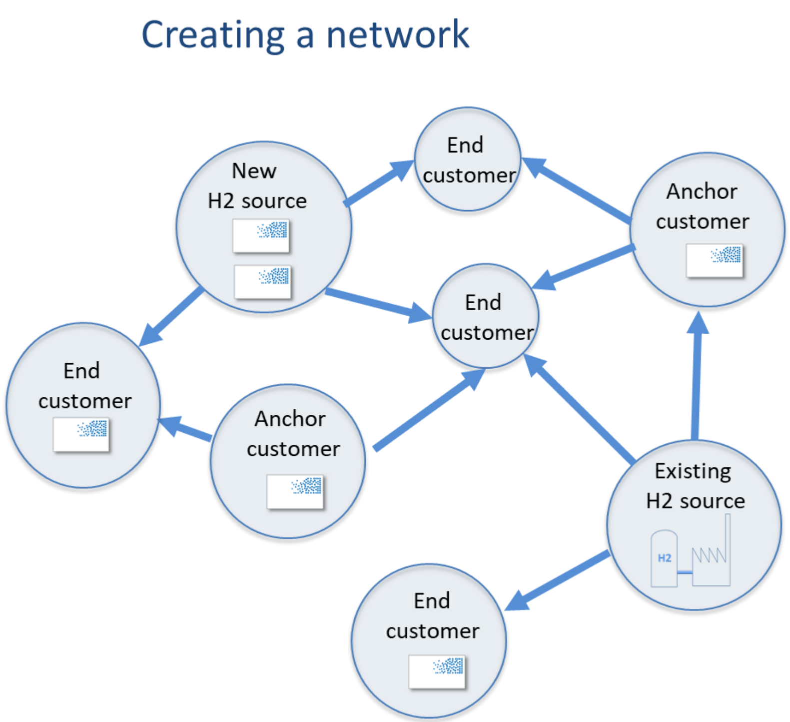


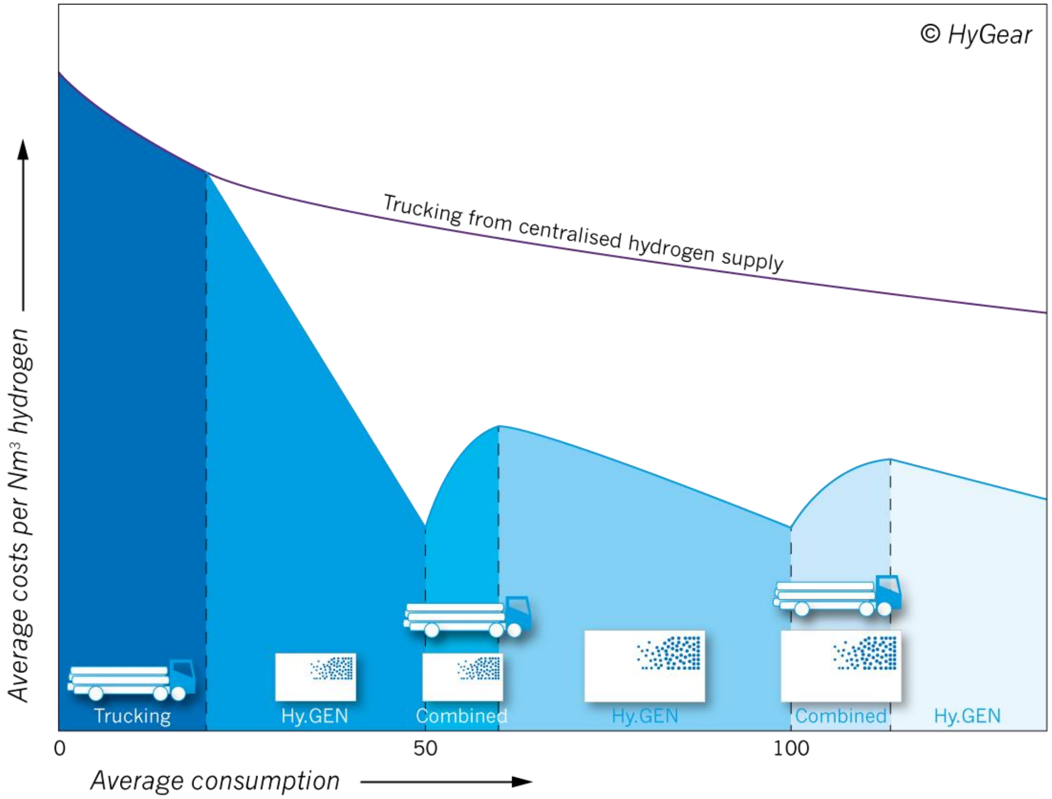
HYDROGEN MARKET



Bron: Air Liquide

THE MERITS OF ON-SITE SUPPLY





ON-SITE HYDROGEN GENERATION TECHNOLOGY EXPLAINED

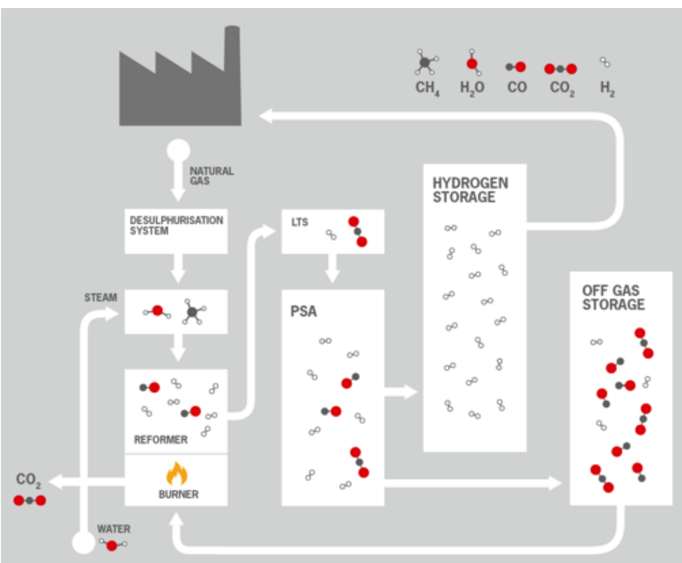
HYDROGEN TECHNOLOGY EXPLAINED

The unique strength of Hy.GEN® SMR-technology:

- Hy.GEN® Steam Reforming needs 0.5 Nm^3 Natural gas per Nm^3 H_2

When compared to other supply methods:

- Electrolysis; that needs 6.5 kWh Electricity per Nm^3 H_2
- Trucking; that needs 40 tons of truck to move 300 kg of gas

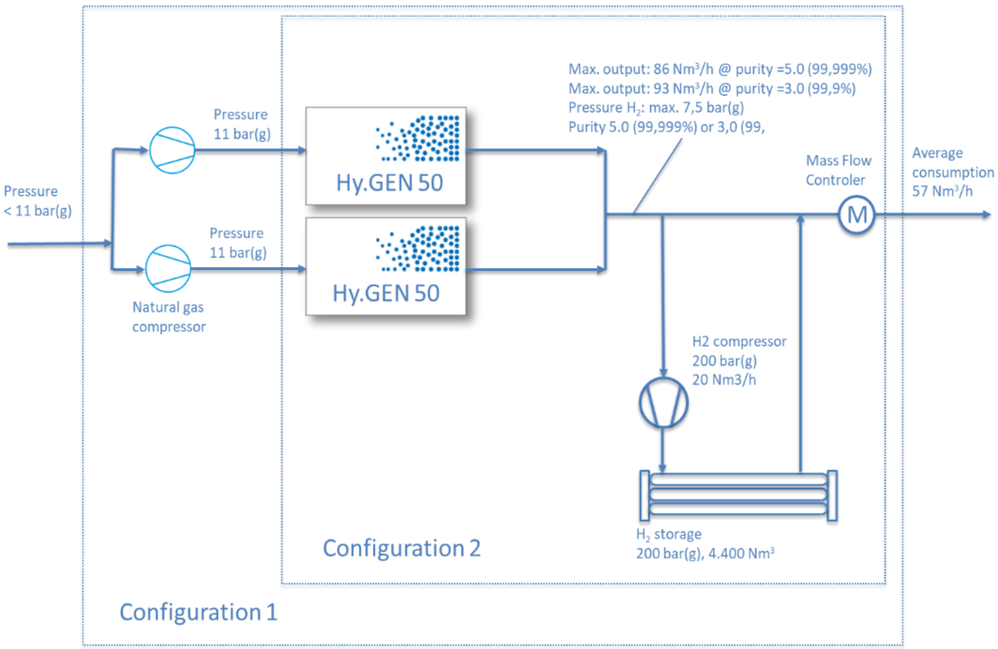


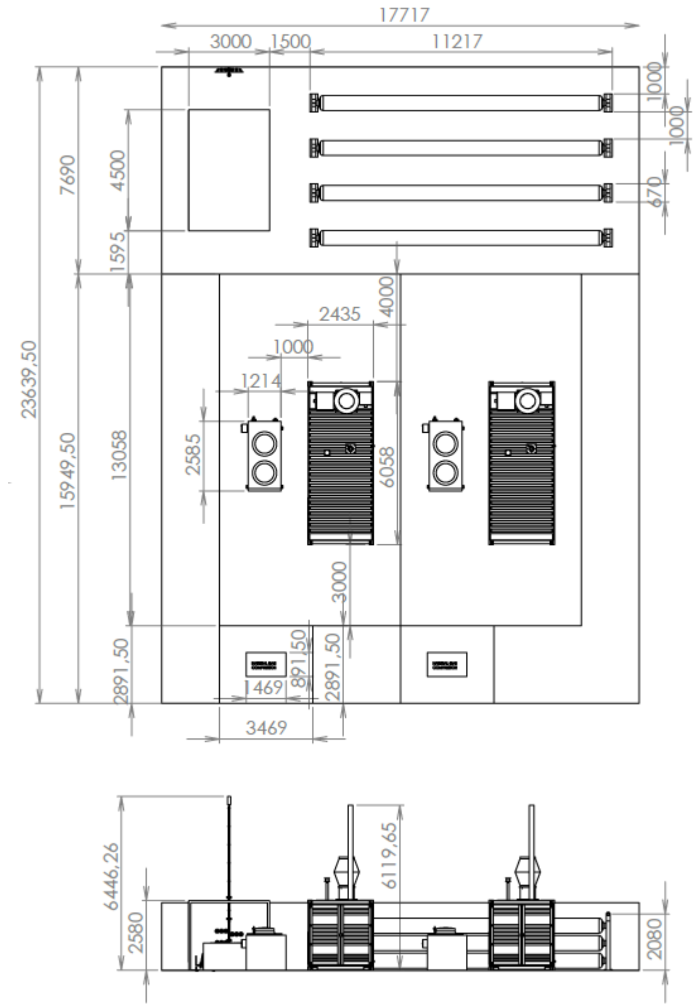
1. Ventilation fan
2. Desulphurisation vessel
3. PSA-vessels
4. Off-gas storage
5. Hydrogen storage
6. Water separator for vacuum pump
7. Vacuum pump
8. Coolant heater
9. Reformate cooler
10. Electronics cabinet
11. Steam generator
12. Reformer unit
13. Low temperature shift
14. Coolant expansion vessel
15. Burner air blower
16. Water purification system

HY.GEN MODELS

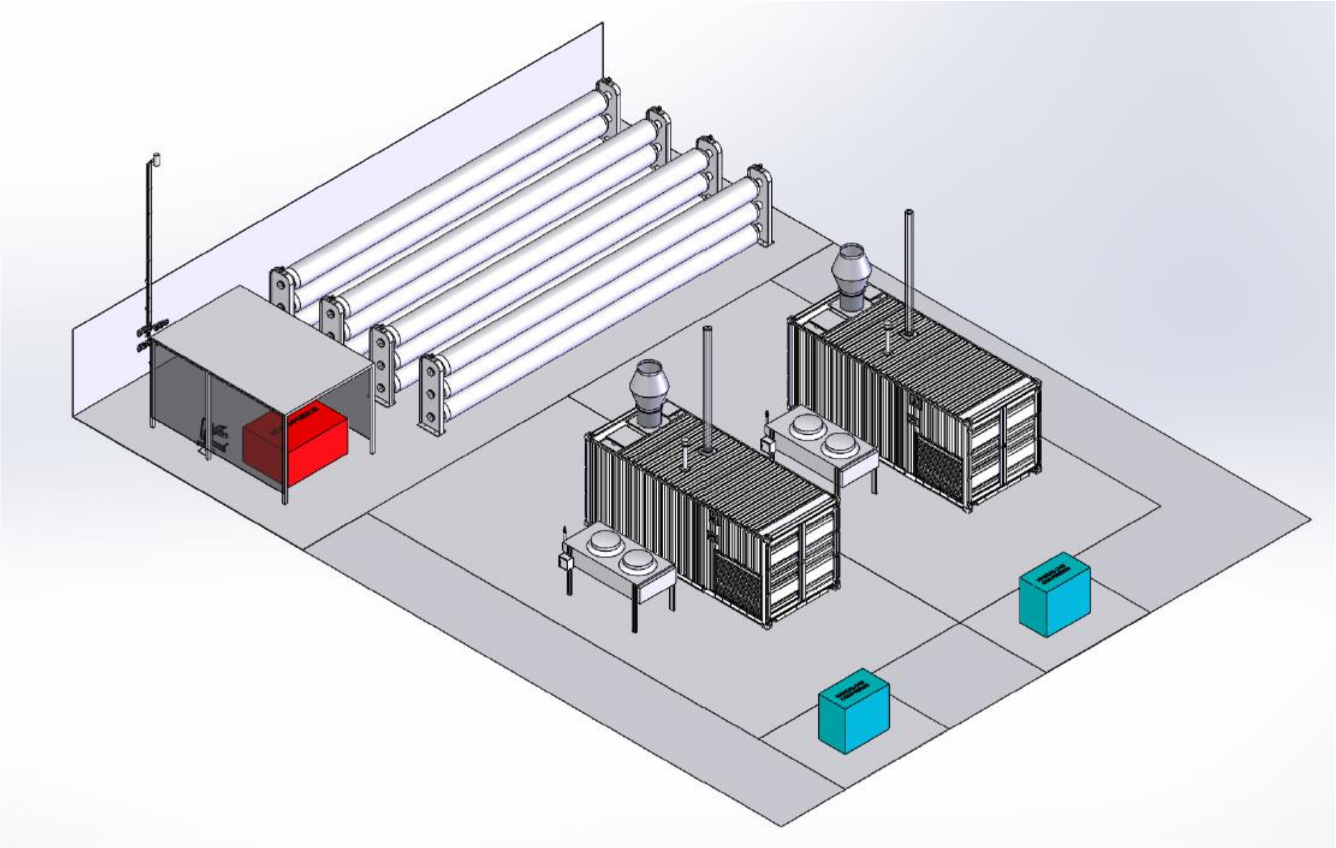
MODEL	Hy.GEN® 50	Hy.GEN® 100	Hy.GEN® 150
OUTPUT			
Nominal H_2 flow	Max. 47 Nm^3/h	Max. 94 Nm^3/h	Max. 141 Nm^3/h
Hydrogen Purity Range	99.5 – 99.9999 %	99.5 – 99.9999 %	99.5 – 99.9999 %
Pressure Range	1.5 – 7.5 bar(g)	1.5 – 7.5 bar(g)	1.5 – 7.5 bar(g)
TYPICAL CONSUMPTION DATA			
Natural Gas	Max. 23 Nm^3/h	Max. 46 Nm^3/h	Max. 69 Nm^3/h
Electricity	12.5 kWe	22.5 kWe	25 kWe
Water	100 l/h	200 l/h	300 l/h
Compressed air	Max. 3 Nm^3/h	Max. 6 Nm^3/h	Max. 9 Nm^3/h
DIMENSIONS			
Size	20 ft.	40 ft.	40 ft.
Weight	6,500 kg	10,000 kg	12,000 kg
OPERATING CONDITIONS			
Start up time (warm)	Max. 30 min	Max. 30 min	Max. 30 min
Start up time (cold)	Max. 3 hours	Max. 3 hours	Max. 3 hours
Modulation (H_2 product flow)	0 – 100 %	0 – 100 %	0 – 100 %
Modulation Reformer (output)	10 – 100 %	10 – 100 %	10 – 100 %
Ambient Temperature Range	-20 °C to +40 °C	-20 °C to +40 °C	-20 °C to +40 °C

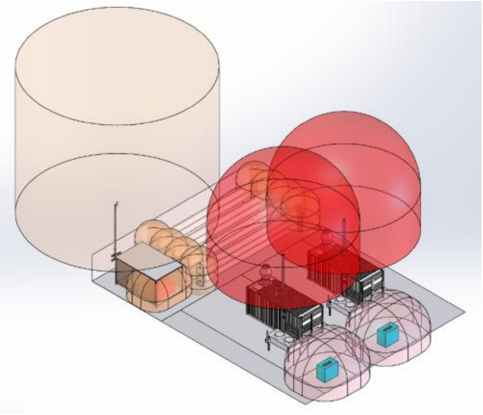
TYPICAL CONFIGURATION GLASS PLANT





TYPICAL CONFIGURATION GLASS PLANT





SAINT GOBAIN L'ARBOC, SPAIN

DUZCE CAM, TURKEY

PHILIPS LUMILEDS TURNHOUT, BELGIUM

WALMART TEXAS, USA

HYGEAR HYDROGEN FILLING STATION IN THE NETHERLANDS

SUMMARY OF KEY BENEFITS

- Industrial Gas supplier in small bulk
- Ability to design, install and operate the supply
- Highest security of supply by on-site generation with trucked back up
- Against the lowest costs due to advanced technologies

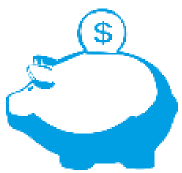
FLEXIBLE CONTRACTING

	BUY	GAS-AS-A-SERVICE (GAAS)
Equipment investment	Customer	HyGear
Infrastructural preparations	Customer	Customer
Installation & commissioning	HyGear	HyGear
Equipment operation	Customer	Customer
Service including system monitoring assistance	Contract option available	HyGear
Maintenance	Contract option available	HyGear

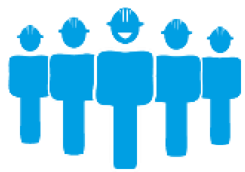
FLEXIBLE CONTRACTING

YOUR BENEFITS:

NO FINANCIAL INVESTMENT

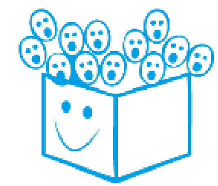


NO ADDITIONAL RESOURCES NEEDED

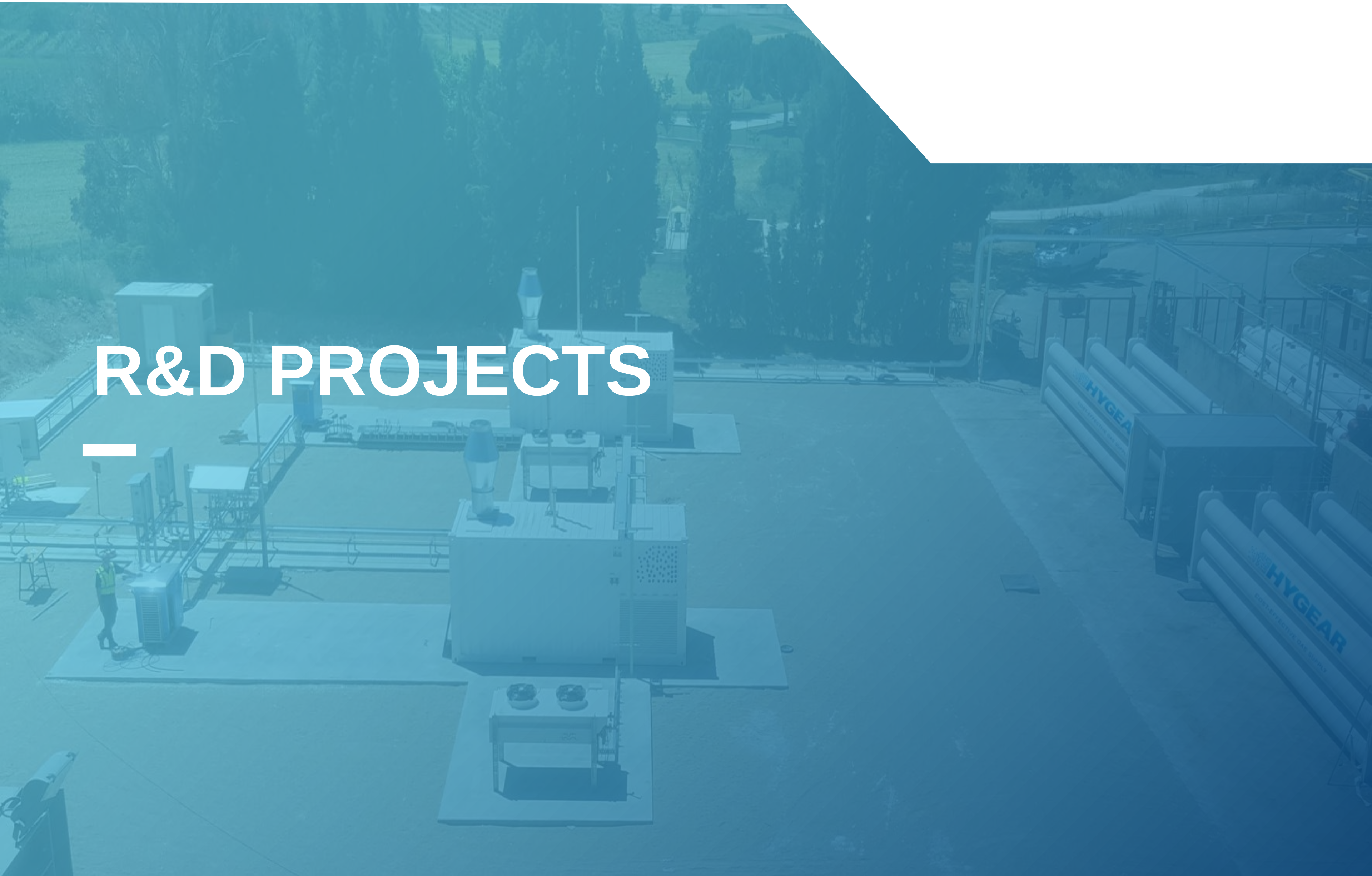


YOU CAN CHOOSE…

NO SURPRISES



R&D PROJECTS



R&D PROJECTS

MEMBRANE PROJECTS

Hy2SEPS2
- H_2 mem+PSA hybrid system

DEMCAMER
- O_2 mem ATR, O2 mem OCM,
  H_2 mem WGS, H_2O mem FTS

REFORCELL
- H2 mem for NG ATR

FERRET
- H_2 mem for flexible feedstock gas ATR

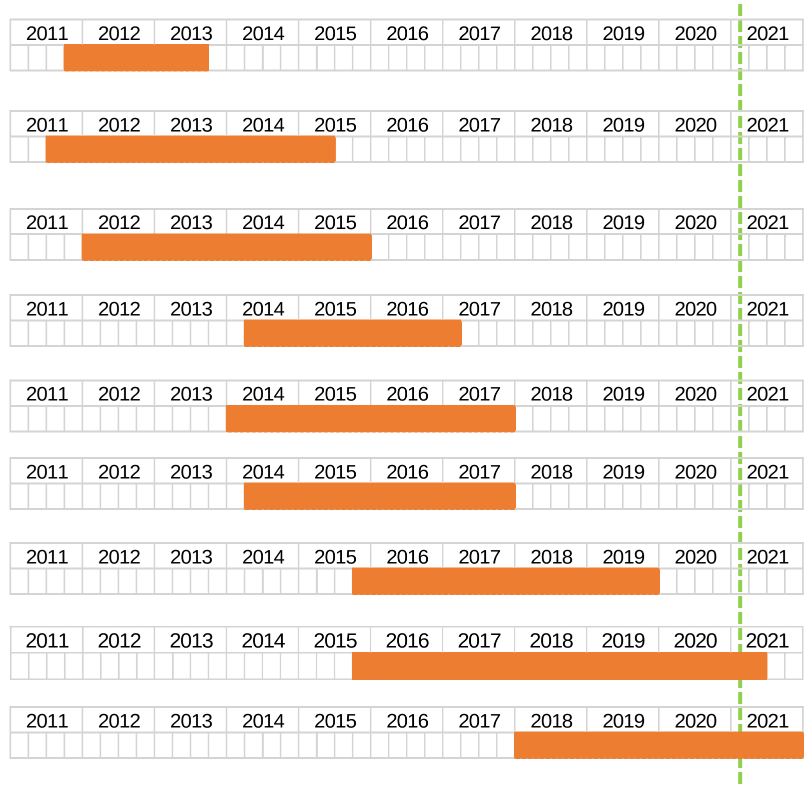
M4CO2
- H_2 mem (pre-comb); CO_2 mem (post-comb)

FLUIDCELL
- H_2 mem for EtOH ATR

MEMERE
- O_2 mem

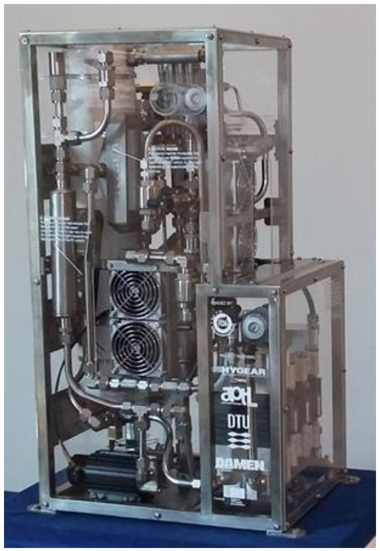
HyGrid
- H_2 mem separation

MEMBER
- H_2 mem (pre-comb); CO_2 mem (post-comb)

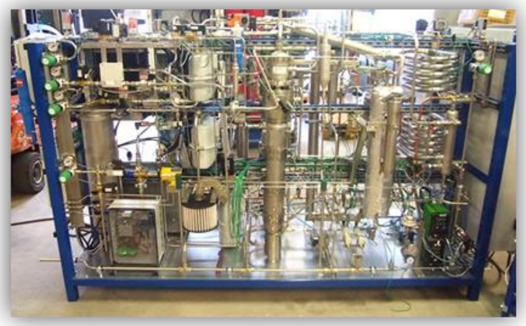


R&D PROJECTS

EXAMPLES



PBI fuel cell system



Membrane reformer system

Gas purification of waste water treatment

PSA systems

Biogas upgrading

Fermentation and hydrogen stripping

Advanced MEMBranes
and membrane assisted procEsses
for pre- and post- combustion CO_2 captuRe

MEMBER

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760944

HYGEAR

Introduction on CO_2 emissions

- CO_2 is the undesired by-product of hydrocarbon conversion processes and the product of combustion in power production, building heating, transportation, etc.

- CO_2 emissions from stationary system come mostly from power production (~80 %), while cement, refinery, steel and petrochemical contribute for about 20 % [1].

- The first objective of CO_2 capture is the decrease of anthropogenic CO_2 emissions. In parallel there is an effort to develop potential CO_2 applications that could, at least in part, economically support the deployment of CCS technologies

PROCESS	CO_2 emissions 10^6 metric ton / year	% on the Total	
Power production	10,539	78.8	~80%
Cement production	932	7.0	~20%
Refineries	798	6.0	
Iron and steel industry	646	4.8	
Petrochemical industry	379	2.8	
Oil and gas processing	50	0.4	
Other sources	33	0.2	

[1] IPCC reports 2018

CO_2 demand and potential

- The potential for CO_2 utilisation is substantial
- Existing uses and demand of CO_2:
- Purification requirements vary widely

Existing uses	Brief description	Future potential non-captive CO_2 demand (MTPA)	Minimum purity
Enhanced oil recovery (EOR)	CO_2 acts as a solvent that reduces the viscosity of oil fields, enabling it to flow to the production well.	30 < demand < 300	90 %
Food	CO_2 used in different applications, including packaging (modified or controlled atmosphere packaging), cooling while grinding powders, food spoilage prevention by acting as an inert atmosphere and dry ice as refrigerant to prolong food storage	~15	99.9 %
Beverages	Carbonation of beverages with high-purity CO_2.	~14	99.9 %
Refrigerants	Used as working fluid in refrigeration plants, especially for industrial air conditioning and refrigeration systems.	<1	99.9 %
Industrial	Used for steel manufacturing, metal working, welding and other applications.	<1	99.5 %
Storage	CO_2 sequestration		95 %

Processes for CO_2 Capture

- In combustion processes CO_2 can be captured via three different routes:
  - Post-Combustion
  - Pre-Combustion
  - Oxyfuel-Combustion

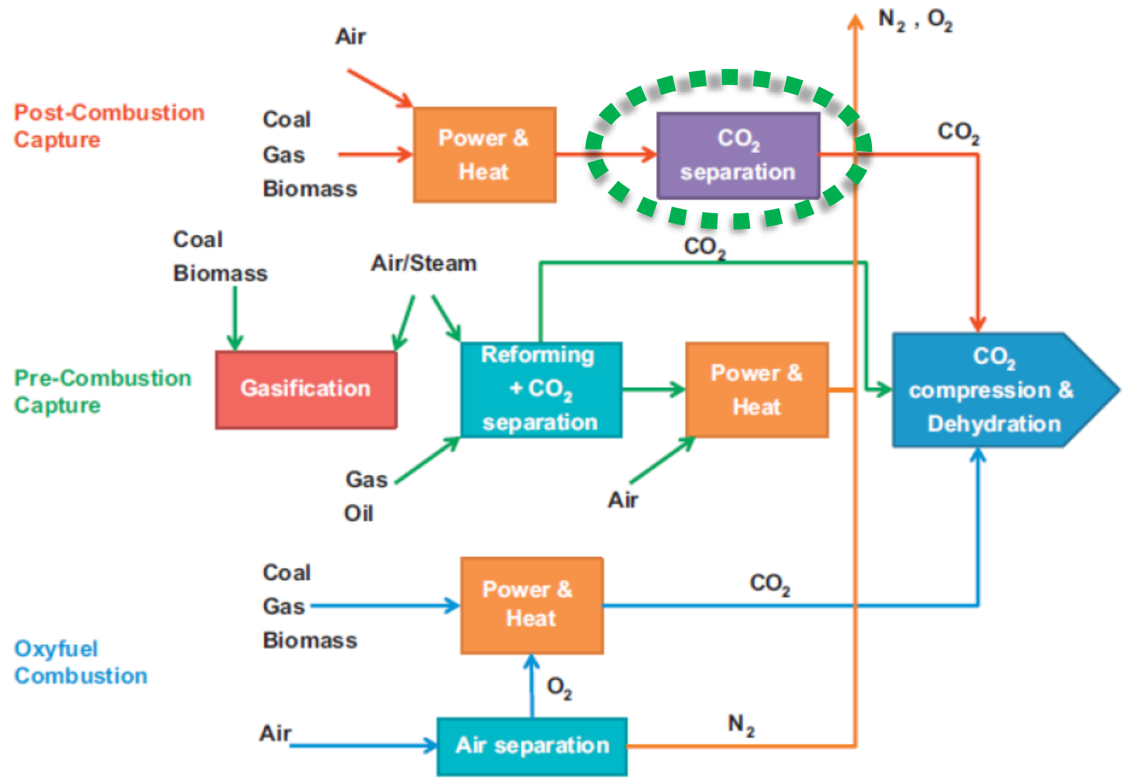


Figure 1. Schematic conceptual representation of CO_2 capture technologies [12].

Benchmark process for post-combustion CO_2 Capture

- At large scale and low CO_2 content in the feed, chemical absorption is the most widespread technology. This is the benchmark technology for the MEMBER project
- It is applied in many industrial units such as ammonia production and gas processing and in some existing CCS applications (mainly aimed at EOR)
- Physical absorption and adsorption are more suitable at smaller scales and/or when CO_2 partial pressure in the feed is sufficiently elevated The absorption/regeneration process (both chemical and physical) is by far the most widespread technology for CO_2 separation from gaseous streams.
- For a detailed description of benchmark technologies and industrial requirements, visit public deliverable D2.2 available at the MEMBER website.

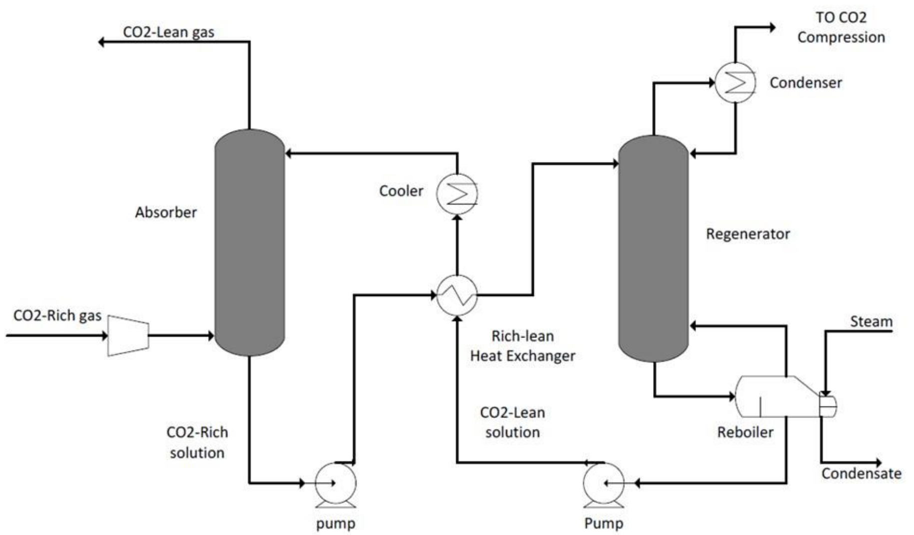


Figure 2. Typical flowsheet of a basic chemical absorption process for CO_2 capture.

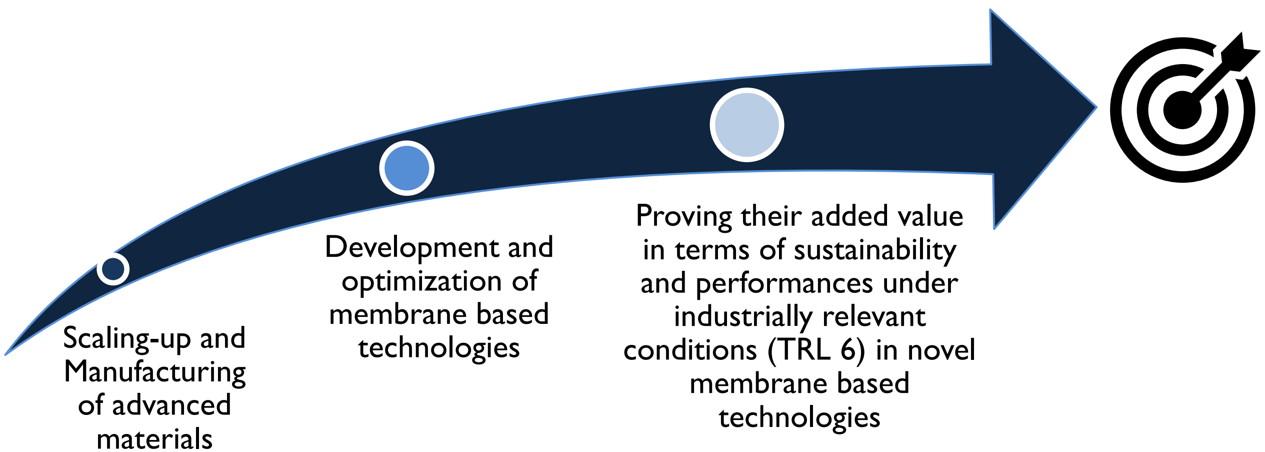
Membrane based CO_2 separation for post-combustion capture

- Perm-selective membranes are thin barriers that allow selective permeation of certain gases
- Driving force for permeation is the CO_2 partial pressure, hence flue gas compression may be required, depending on the gas conditions
- In MEMBER we develop hollow fiber (HF) membrane modules permeable to CO_2, offering important advantages, such as high packing density (>10,000 m^2/m^3), resistance to high pressure difference, and contained fabrication costs
- For post-combustion CO_2 capture (CO_2/N_2 separation) thin film Pebax polymer based composite hollow fibers are being prepared by dip coating of porous hollow fiber supports. Metal Organic Framework (MOF) will be in the outside coating selective layer

HYGEAR

MEMBER Objectives

- The main objective of the MEMBER project is the scale-up and manufacturing of advanced materials and technologies, aimed to reduce the cost of CO_2 capture.



Outperforming current technologies for pre- and post-combustion CO_2 capture in power plants as well as H_2 generation with integrated CO_2 capture and meet the targets of the European SET plan.

- Each solution is going to be demonstrated through the operation and test of a prototype
- Scale-up issues are addressed during the project and a Business Plan is prepared for the industrial application of each technology.

MEMBER Objectives

- Reference and Target Performance and Cost for the MEMBER processes
- The target CO_2 purity for MEMBER process is 95 %.

	Reference Technology	Reference CCR [%]	Reference Cost of CO_2 [€/ton]	MEMBER Targets for CCR [%]	MEMBER Targets for Cost of CO_2 [€/ton]
Pre-comb. Power (IGCC)	Absorption by SELEXOL	90.9	33.0	90	< 30
Post-comb. Power (Coal)	MEA absorption	88.1	54.3	90	< 40
Hydrogen via SMR (NG) +CO_2 pre-comb. capture	MDEA absorption	56	47.1	90	< 30
Hydrogen via SMR (NG) +CO_2 post-comb.capture	MDEA absorption	90	69.8	90	< 30

MEMBER Objectives

Targets

Prototype A

Pre-combustion capture in power plants using MMMs at the 2 MWth biomass gasifier of CENER (Spain) aimed for BIOCCS demonstration.

CCR > 90%

Capture Cost < 30 €/ton

Prototype B

Post-combustion capture in power plants using MMM at the 8.8 MW CHP facilities of Agroger (GALP, Portugal).

CCR > 90%

Capture Cost < 40 €/ton

Prototype C

Pure hydrogen production with integrated CO2 capture using MA-SER at the IFE-HyNor (Norway) under the supervision of ZEG POWER.

CCR > 90%

Capture Cost < 30 €/ton

HYGEAR

System demonstration at industrial site

➤ Demo Site: AGROGER CHP plant - property of Galp Energia - Portugal

- Galp Energia is a vertically integrated multi-energy operator operating in the oil and natural gas business and as a producer and seller of electricity for industrial and home consumption.

- AGROGER CHP plant consists of 2 sets of natural gas fuelled power-generators providing up to 8.8 MWe of power, plus heat to users in the area

System requirements

- Main materials and process targets:

Target MMM	Value	Unit
CO_2 permeance	300	GPU
CO_2/N_2 selectivity	70	-
Membrane area	10	m^2
Design pressure	7	bar(g)
Membrane cost	<100	€/m^2
Target process	**Value**	**Unit**
CO_2 recovery	90	%
CO_2 purity	95	%

System requirements

Other design conditions:

- Feed flow 10 Nm^3/h.
- Atmospheric supply pressure
- Composition:

Species	% molar
CO_2	5.8 %
H_2O	3.7 %
O_2	10.0 %
N_2	80.5 %
Total	100 %

- Selectivities:

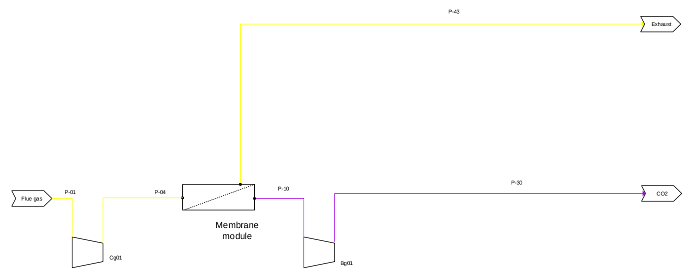
CO_2/H_2O	1
CO_2/O_2	28
CO_2/N_2	**70**

- 1 or 2 stage layout

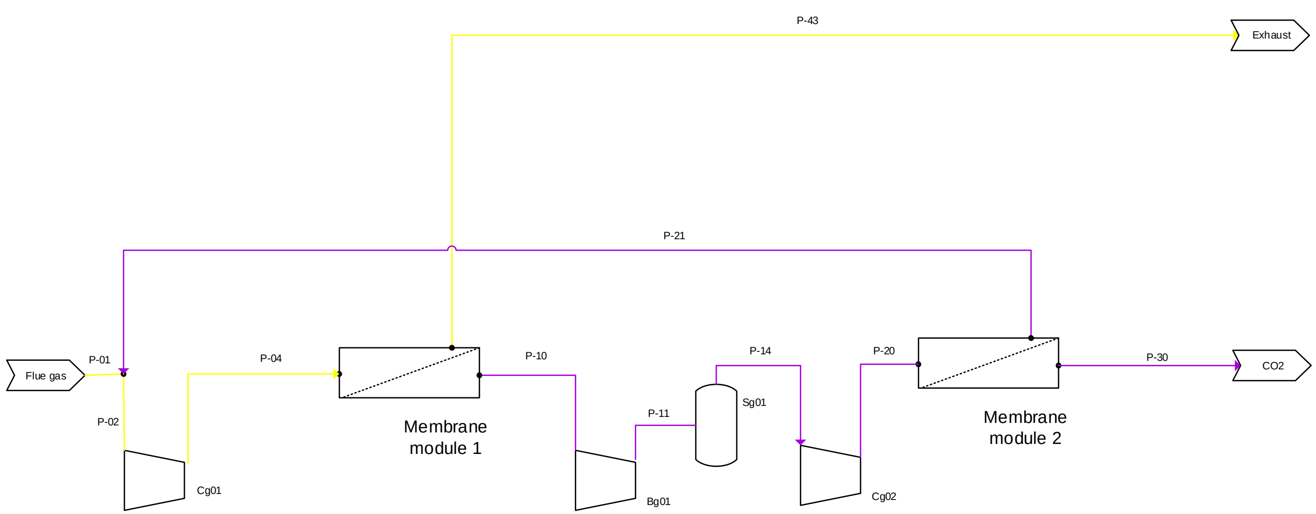
System design and development

Modelling different layouts

- Single stage layout;
  - CO_2 purity target not reached, neither without nor with recirculation



- Dual stage layout
  - CO_2 separation membrane #1 = 94 %
  - CO_2 separation membrane #2 = 57 %
  - Vacuum pump on permeate membrane #1



System design and development

Modelling sensitivity to membrane permeance

Permeance (GPU)	CO_2 rec.	CO_2 purity
300 (nominal target)	>90 %	>90 %
200	86 %	>90 %
100	67 %	>90 %

* Cases with constant pressure at 4 bar

- CO_2 recovery is reduced if permeance decreases
- Purity is not compromised
- Countermeasure would be to increase operating pressure to maintain CO_2 recovery

Permeance (GPU)	CO_2 rec.	CO_2 purity	Pressure membranes stages # 1/2 (bar)
300 (nominal target)	>90 %	>95 %	7 / 6
200	>90 %	>95 %	9 / 9
100	>90 %	>95 %	14 / 14

System design and development

Modelling sensitivity to membrane selectivity

- Selectivity S [CO_2/N_2]

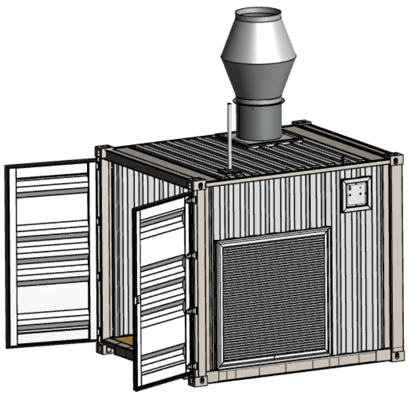
S [CO_2/N_2]	CO_2 recov.	CO_2 purity
70	90.6 %	93.5 %
40	90.6 %	90.0 %

* S to N_2 and H_2O left unchanged. Cases at 4 bar.

- Purity is affected by a decay in selectivity

Conclusions and final remarks

- The prototype for post-combustion CO_2 capture will be demonstrated in an industrially relevant environment, allowing validation of the performance and stability of the technological solutions and materials.
- Prototype design with two stages meets targets of CO_2 purity >95 %, and recovery >90 %
- Membrane module stage #2 is smaller than membrane module stage #1
- Maximum operating pressure 7 bar(g)
- Selectivity is very important to reach the purity targets
- In case of lower permeance, we need to increase the operating pressure
- System design is finalised, and assembly is ongoing.
- System will be installed in 10 ft container



Design and development of a membrane based post-combustion CO_2 capture system

Workshop on CCUS
16-17 / 02 / 2021

Thank you for your attention

https://member-co2.com/

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