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VTT

Public Final report

Decarbonate Co-Innovation project

Converting cost to revenue

www.decarbonate.fi

21/06/2022 VTT – beyond the obvious

Teollisuuden ilmastovaikutusten pienentäminen hiilineutraalin energian ja kiertotalouden keinoin – Decarbonate

Business Finland Co-Innovation project
Dnro 2363/31/2019

June 2022. Authors: Eemeli Tsupari, Kirsi Korpijärvi, Juho Kauppinen, Toni Pikkarainen, Timo Leino, Pekka Simell, Mikko Lappalainen, Iris Winberg, Oona Katajisto, Sampo Mäkikouri

Project's objective

- To test and develop selected industrial CO_2 capture and utilisation solutions towards commercial scale

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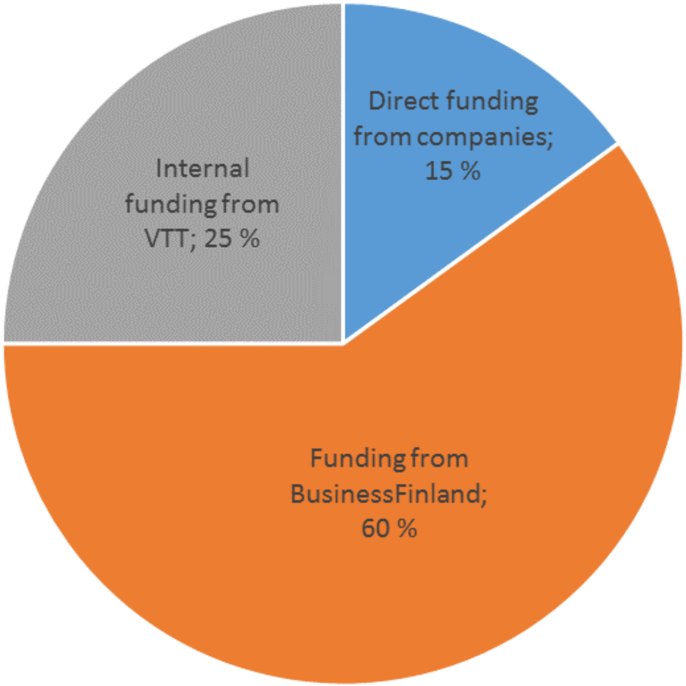
The public research project in numbers

- 36 months (10/2019 – 03/2022)
- 11 industrial partners
- 1.2 M€
  > 2 principal scientists
  > 7 senior scientists
  > 7 research scientists
  > 1 senior technician
  > 4 unique pilot facilities + operators



BUSINESS FINLAND

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Strong consortium

Co-funding partners	BF-supported projects	In-kind-partners
ANDRITZ	KUMERA	CarbonReUse
FINNSEMENTTI A CRH COMPANY	KELIBER	WETEND Technologies
SSAB		INERATEC
Nordkalk		DECARBONATE
st1		
UPM		

Power sector is ”easy” to decarbonate

- Followed by heating (heat pumps) and road transport (electric vehicles)

- Highlights the importance of CO_2 from industries
  - **Cement&lime and iron&steel the most important**

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2.9 Gt
Iron & steel

3.0 Gt
Cement

TOGETHER THESE SECTORS ACCOUNT FOR 40 % OF INDUSTRIAL EMISSIONS

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Difficult to avoid, easy to capture

$$CaCO_3 + heat = CaO + CO_2$$

Shifting from fossil fuels to electricity decrease the amount of CO_2 by roughly 50%

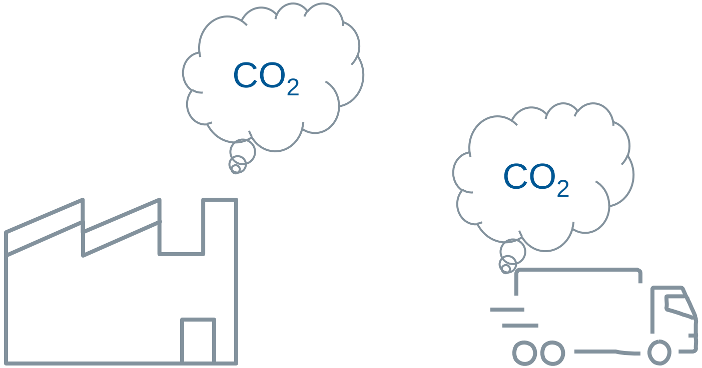
Almost 100% concentration!

CO_2 as a product

- Several existing usages
  - Average price in Finland
    - 2018: 97 €/t
    - 2019: 96 €/t
    - 2020: 96 €/t
- But market is small comparing to CO_2 emissions
  - Finnish market about 200 ktCO_2/a
- Largest potential for growth by Power-to-X (PtX)

Effective tool for climate change mitigation

Now:



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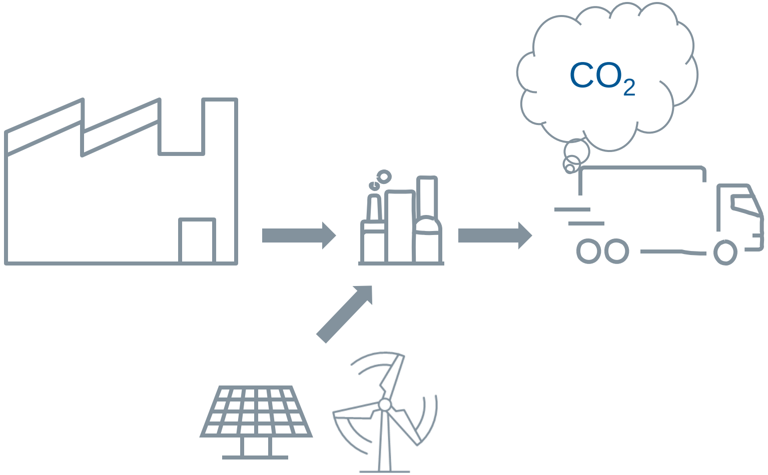
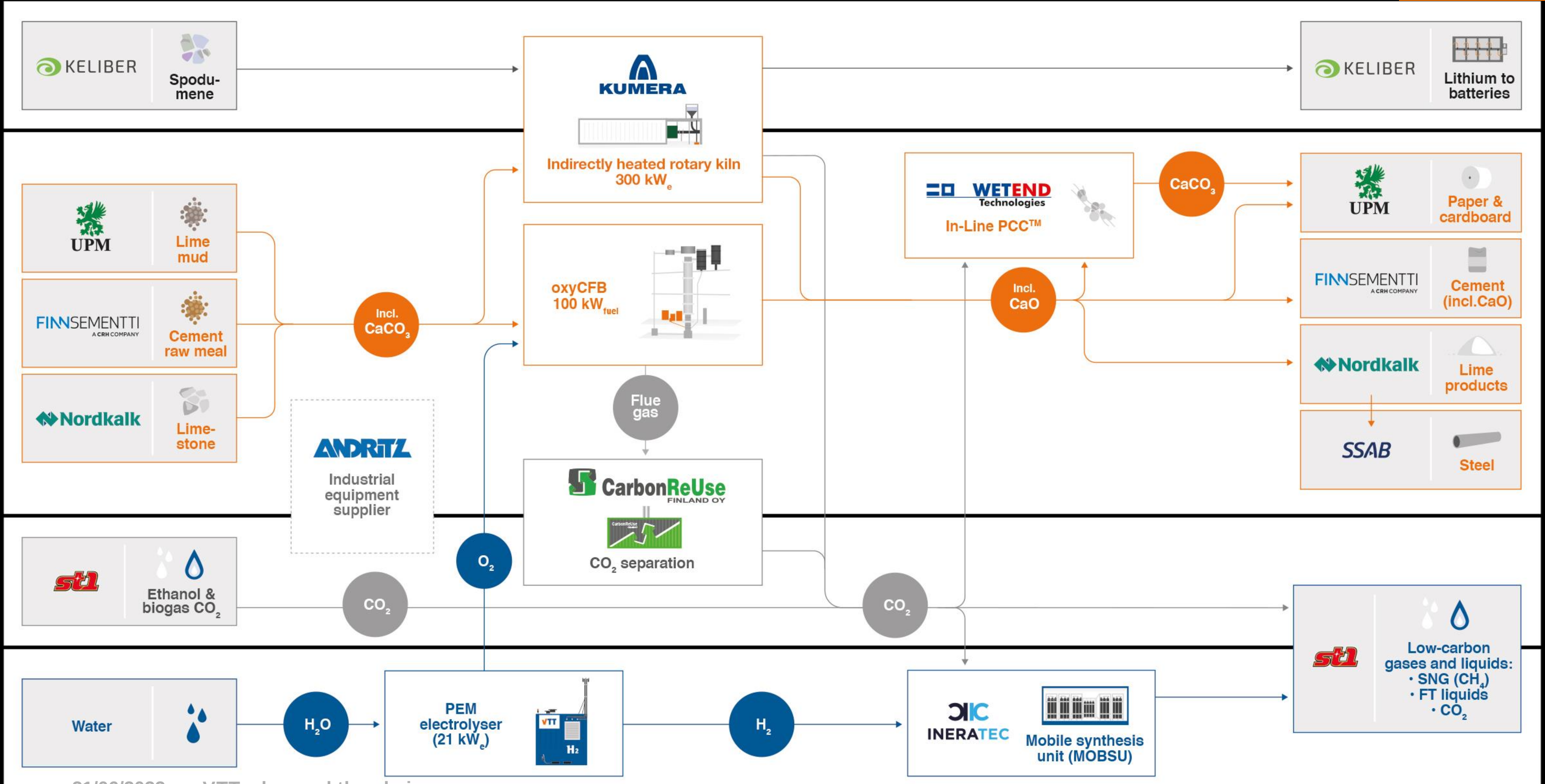


DE|CARBONATE value chains



Project work packages

	WP leader
WP1 Commissioning of indirectly heated rotary kiln	**Juho Kauppinen**
WP2 Oxyfuel experiments by VTT's CFB	**Toni Pikkarainen**
WP3 Rotary kiln experiments	**Timo Leino**
WP4 Synthesis experiments	**Pekka Simell**
WP5 Electrolysis (PEM)	**Mikko Lappalainen**
WP6 Business opportunities	**Iris Winberg**
WP7 Dissemination and international co-operation	**Sampo Mäkikouri**
WP8 Project coordination	**Kirsi Korpijärvi**

Project manager: **Eemeli Tsupari**

WP1: The commissioning of VTT`s Electrically heated mobile rotary kiln research facility (ELMO)

WP1 Tasks

- Clearance of warehouse
- Cooling water piping
- Electric cabling
- Container support structures
- Process exhaust piping
- Measurement equipment installation
- Warm measurement container

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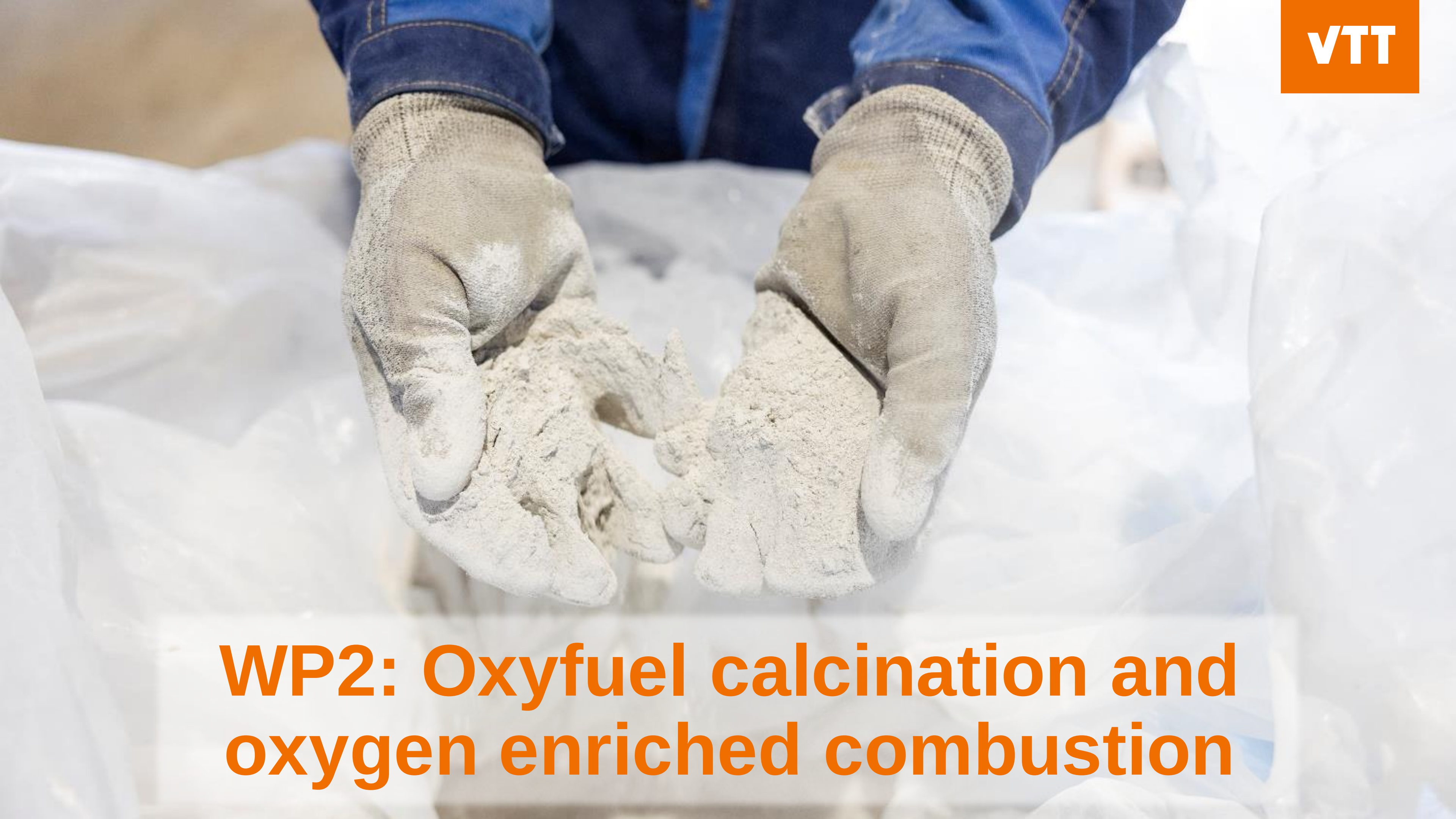
Selected pictures from WP1

Excavation work for cabling and water

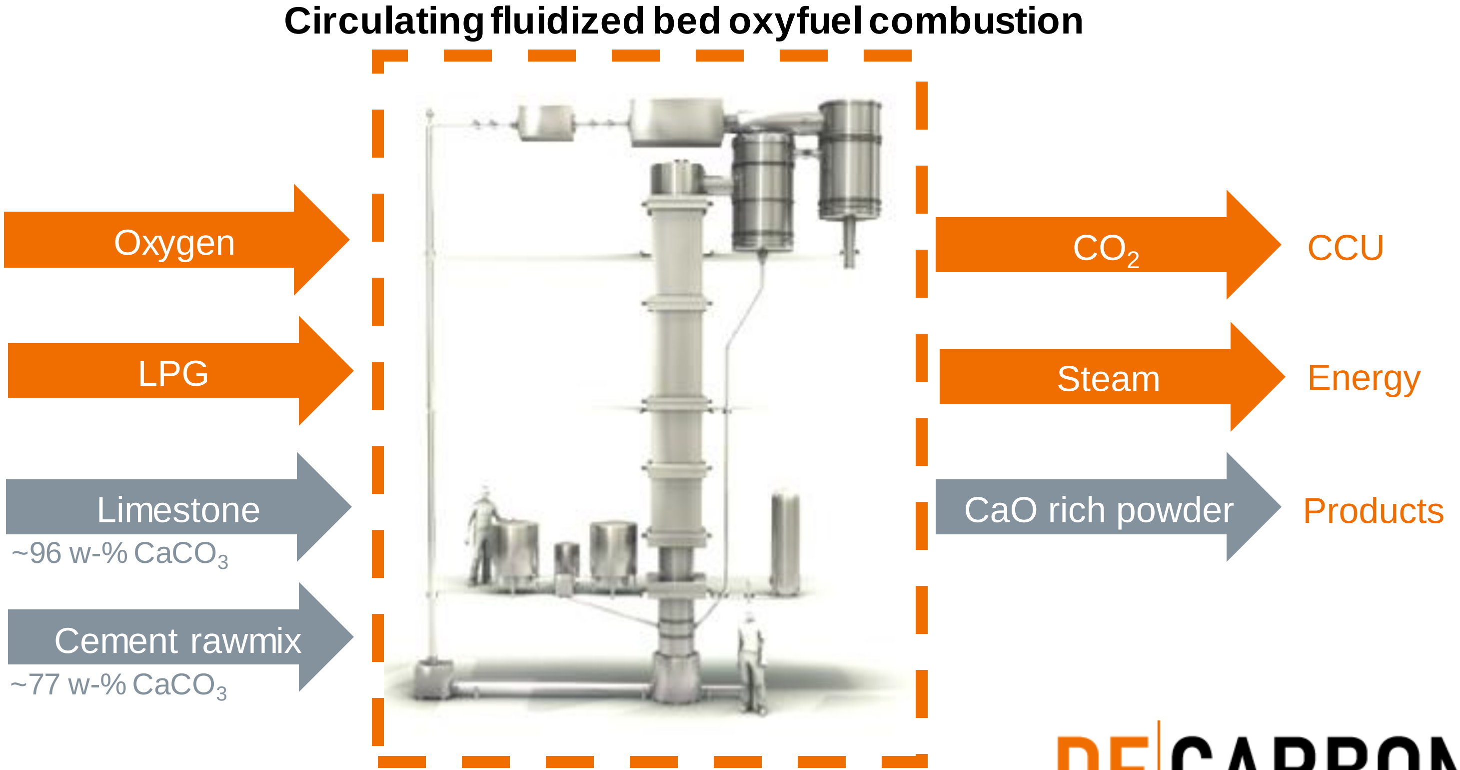
The kiln container was moved to correct position with two cranes (another crane is in the building)

One of the first pictures on the installed kiln



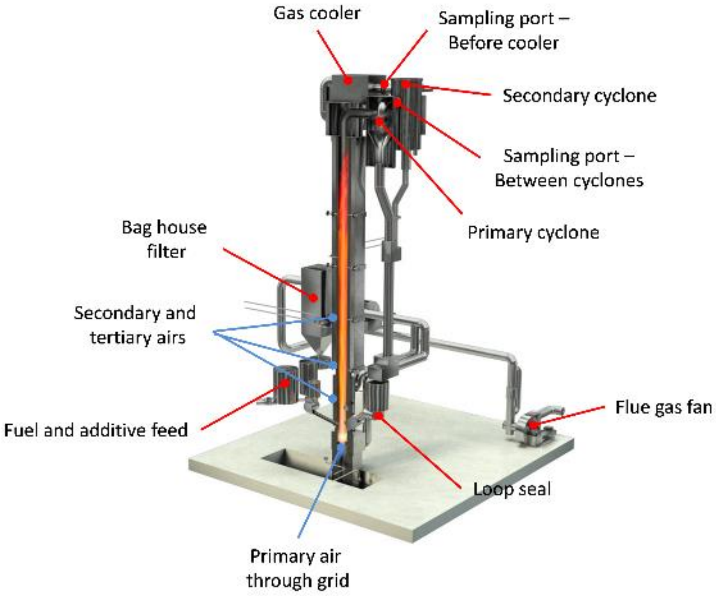
WP2: Oxyfuel calcination and oxygen enriched combustion

WP2: Setup for oxyfuel calcination



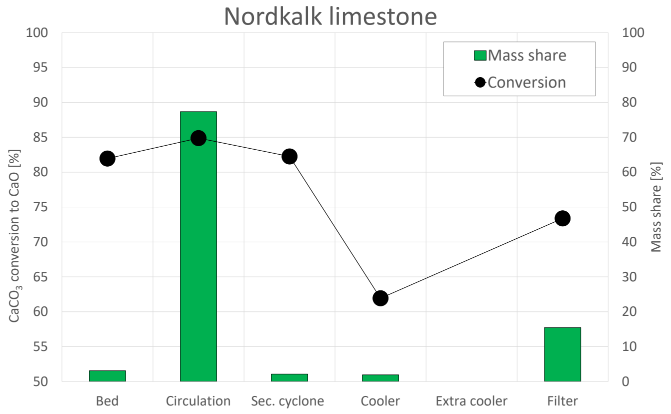
Oxyfuel calcination

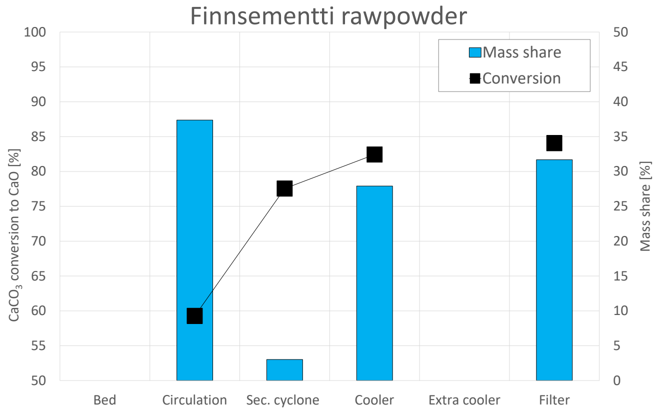
- Oxyfuel CFB pilot was operated successfully to produce CaO-rich ash streams and CO_2-rich flue gas
  - Operational challenges were observed, especially related to ”sticky” behaviour of CaO (and probably some recarbonation)
- Conditions were favourable for calcination of $CaCO_3$ to CaO in the hot loop
  - In downstream the flue gas path more risks for recarbonation due to decreasing temperature in high CO_2 atmosphere



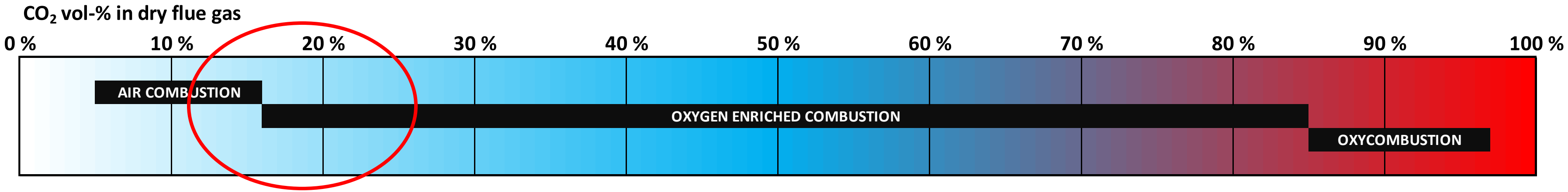
Results from oxyfuel calcination

- $CaCO_3$ conversion to CaO was fairly good (note: VTT's CFB is not designed for calcination)
  - Nordkalk limestone: 85% conversion to 80% mass share (bed and circulation)
  - Finnsementti rawmix: 83% conversion to 63% mass share (fly ash)
  - Studied operational parameters had only small effect on $CaCO_3$ to CaO conversion
- High CO_2 concentration (~90 vol-%) in the flue gas was reached
  - Other flue gas main species were
    - N_2 (8-9 vol-% dry) originating from purge gas and air leakages, and
    - residual O_2 (1-2 vol-% dry)





Oxygen enriched combustion



An example:

300 MW fuel power CFB
Spruce bark (moisture content 40%)
O_2 3.5% in wet flue gas

Air combustion

→ CO_2 **16%** in dry flue gas

Oxygen enriched combustion
Case: 100 MW electrolyser
= 16000 kg/h O_2

→ CO_2 **18.5%** in dry flue gas

Focus of the tests:
to replace part of the combustion air with electrolyser O_2 mixed to recirculated flue gas → How much the CO_2 capture process improves

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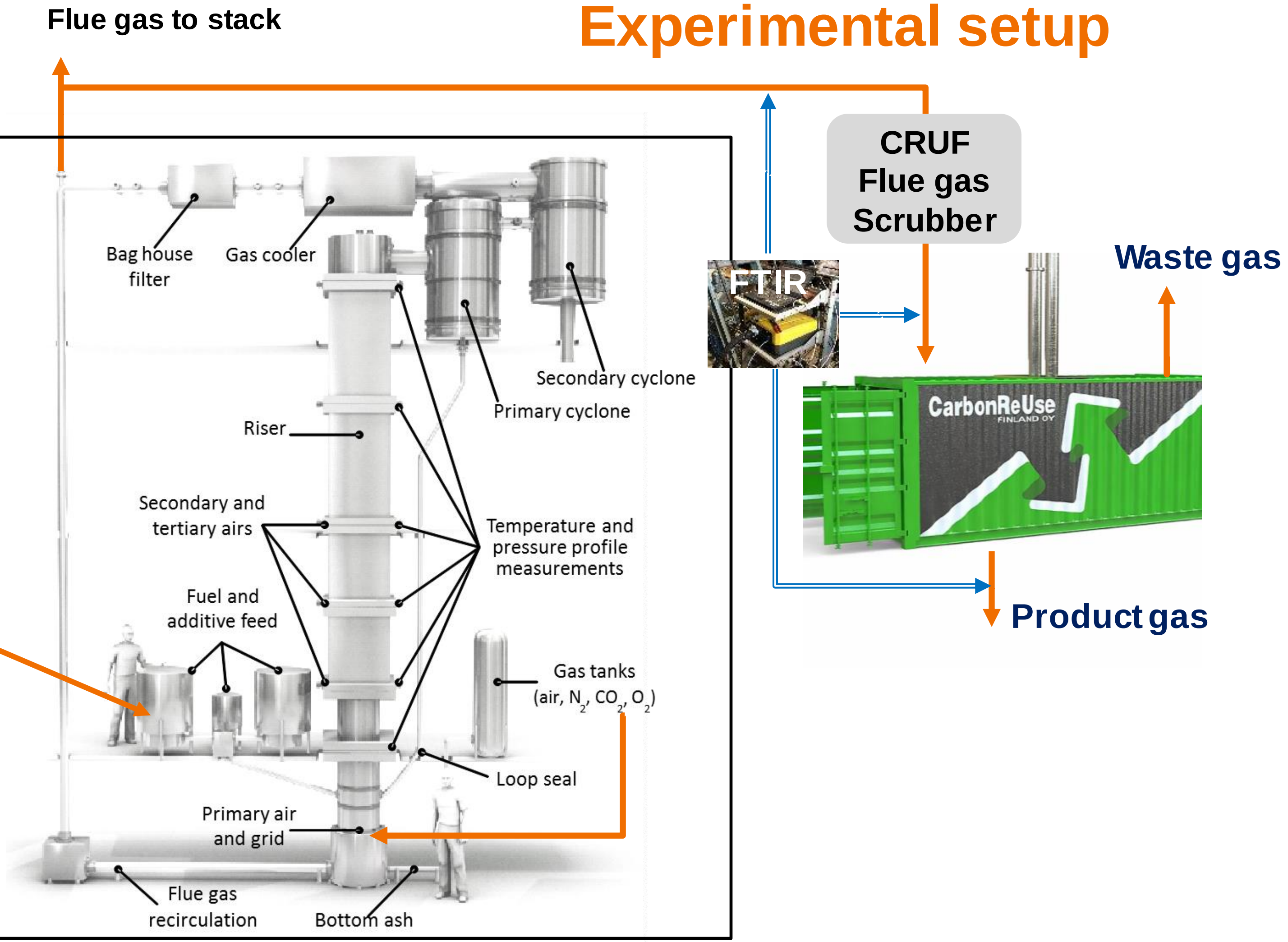
Experimental setup

Wood chip combustion in CFB

Part of the combustion air replaced by O_2 + recirculated flue gas



Experimental setup

Piloting site

Juho & Juha monitoring the measurements

Flue gas line from the CFB-pilot to the capture containers

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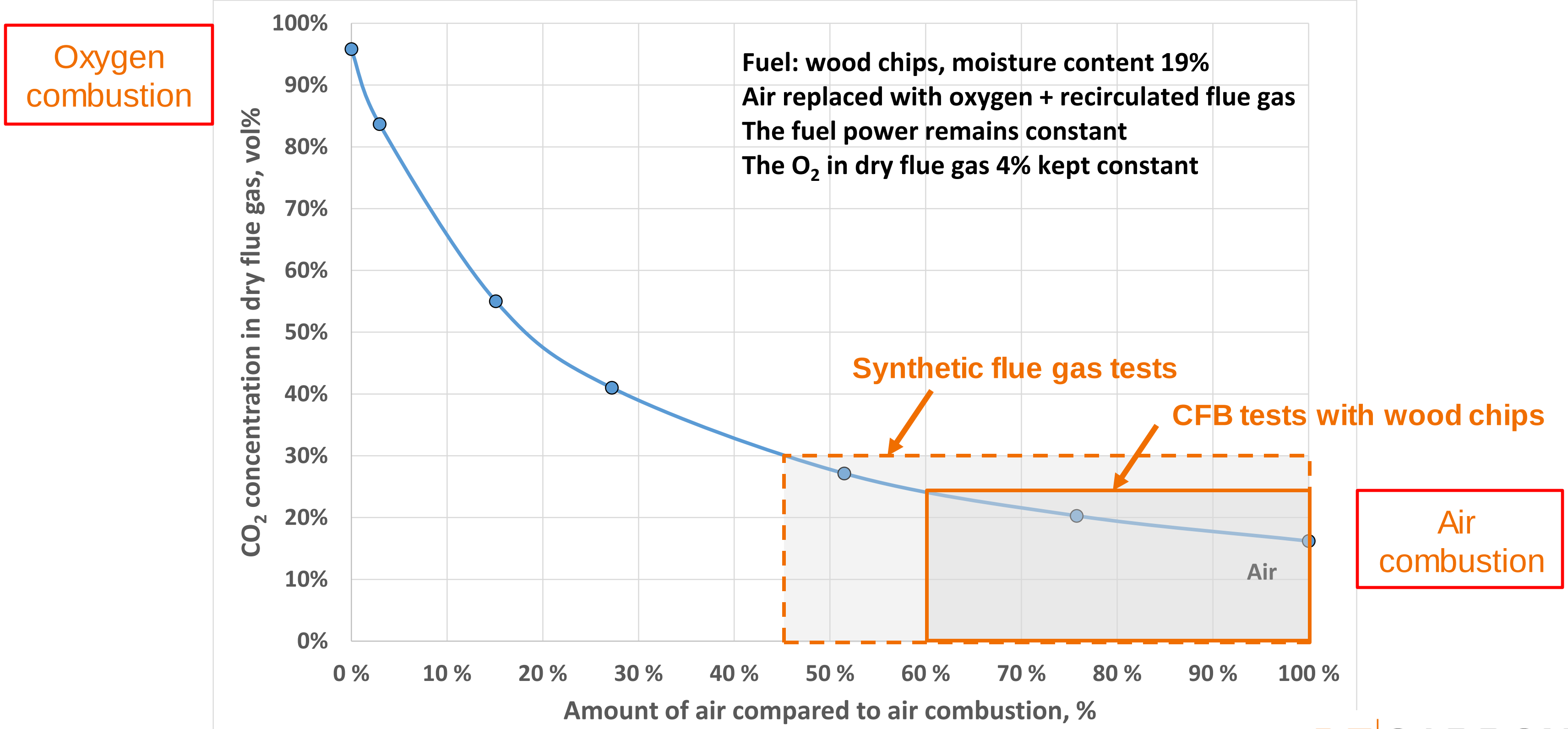
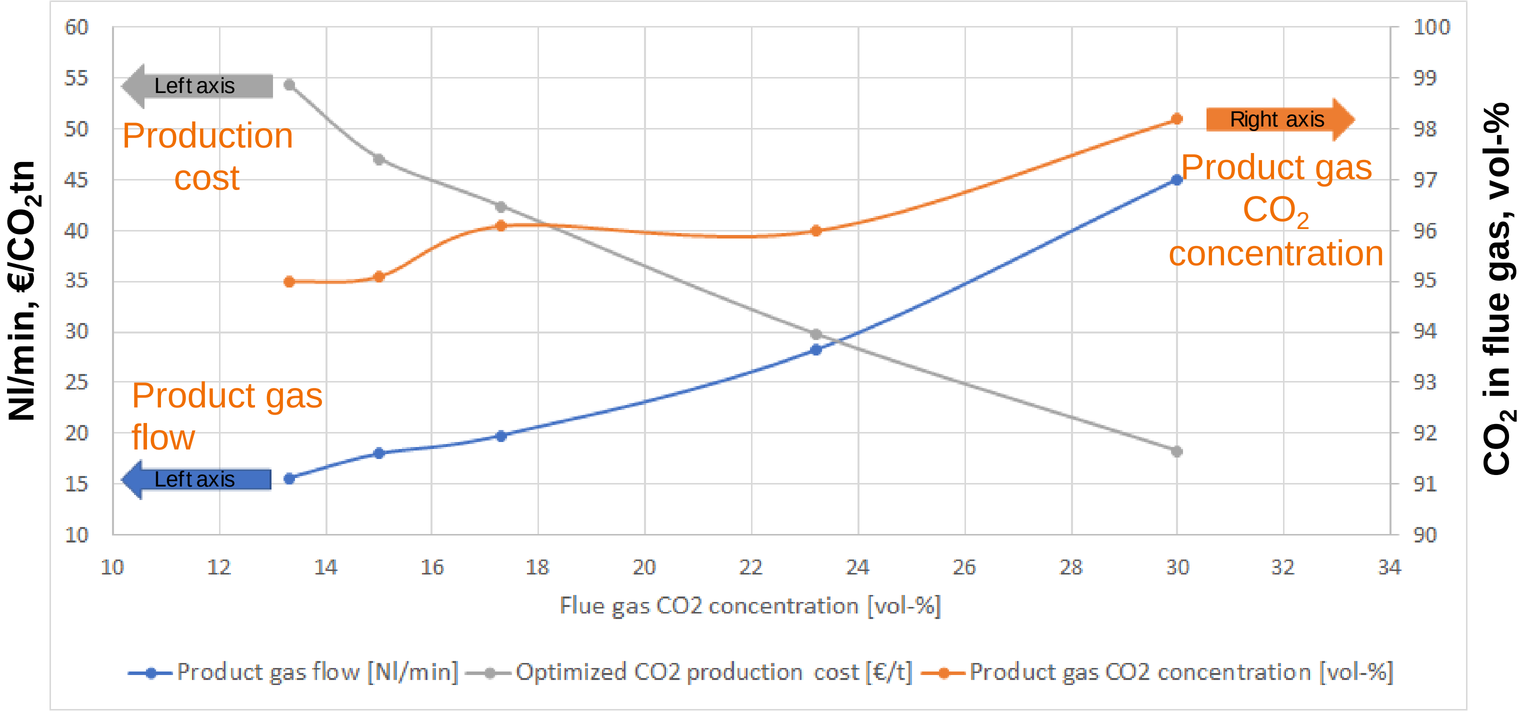
Transition from air to oxygen combustion = oxygen enriched combustion



Results by CarbonReUse Finland

Electricity price 45 €/MWh in calculations



Even a small increase in flue gas CO_2 concentration decrease the CO_2 capture cost as more product CO_2 can be separated from the input flow

WP3: Indirect calcination

Tests in laboratory scale drum (Ø 60mm, L 2,3m)

Test matrix consisted of

- Materials: limestone, cement raw meal, lime mud
- Temperatures: 875 – 975 °C
- Atmosphere: air, CO_2, H_2
- Pressure: normal vs. vacuum

Main results:

- Over 95% calcination degree in air atmosphere
- Higher calcination degrees in vacuum and H_2 compared to normal pressure CO_2 atmosphere
- Main challenge ring formation

Tests in pilot scale drum (Ø 0.54m, L 9m)

Test matrix consisted of

- Materials: limestone & cement raw meal
- Temperatures: 875 – 1050 °C
- Drum rotation: 1 – 4 rpm

Main results:

- Up to 98% calcination degree
- Over 90 vol-% CO_2 in offgas

→ Good basic setup found, more tests needed to fine-tune the product quality

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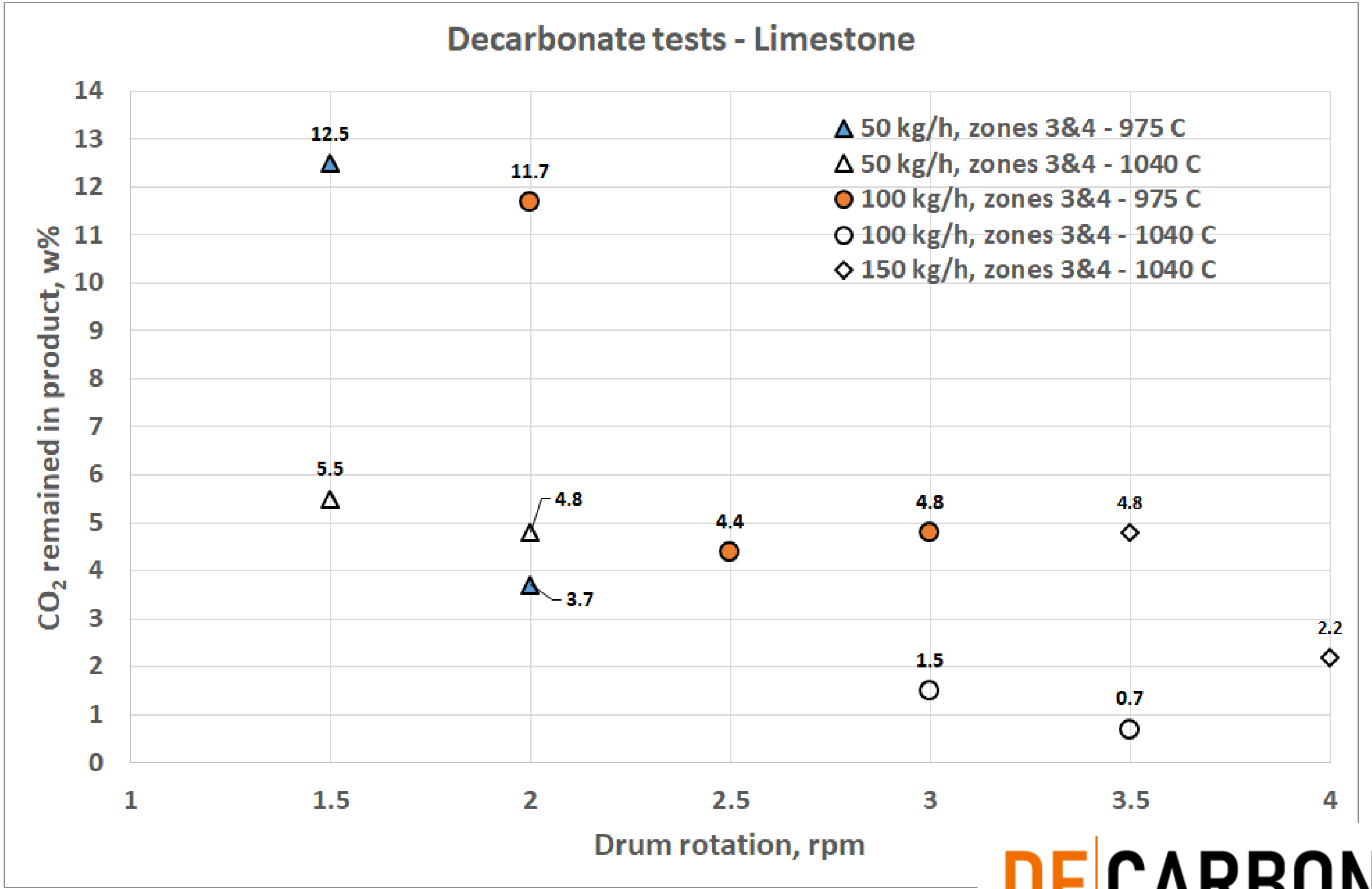

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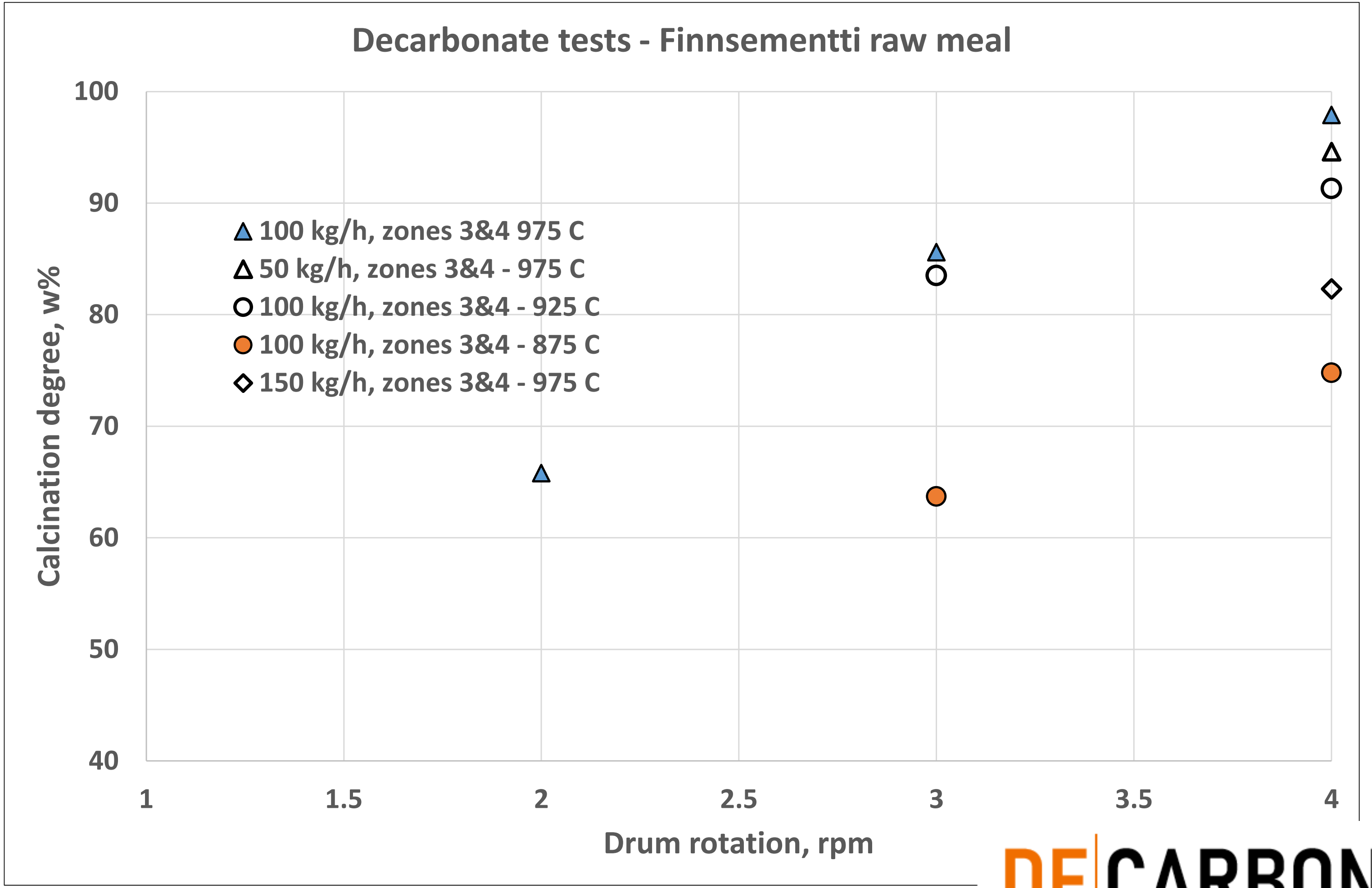

Decarbonate tests - Finnsementti raw meal
100 kg/h, zones 3&4 975 C
50 kg/h, zones 3&4 - 975 C
100 kg/h, zones 3&4 - 925 C
100 kg/h, zones 3&4 - 875 C
150 kg/h, zones 3&4 - 975 C
Calcination degree, w%
100
90
80
70
60
50
40
1
1.5
2
2.5
3
3.5
4
Drum rotation, rpm

WP3 Conclusions

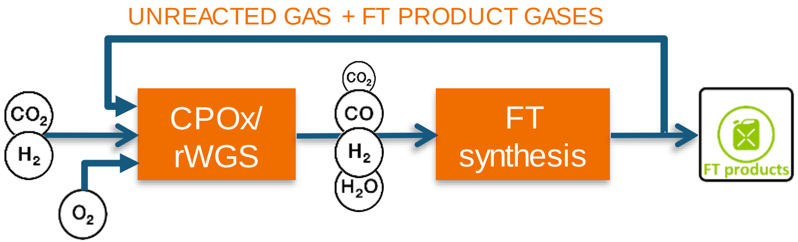
- Promising results from first experiments
  - Increased drum rotation enhances heat transfer and calcination
  - *“It’s exciting to see properties of CaO produced in the best experiment points are very near to product-grade burnt lime.” Erkka Uuttu, Energy Manager, Nordkalk*
  - *“The raw meal of cement production was successfully treated in the trial runs to an intermediate product which is fully calcined but not yet reacted with silica, which is exactly what is wanted to achieve in calciner.” Mathias Frankenhaeuser, Technical Manager, Finnsementti*

- Offgas CO_2 concentration can be controlled and increased in future experiments and in larger scale. Offgas is good feedstock for further purification.

WP4 Synthesis of CO_2 to hydrocarbons

FT-Synthesis

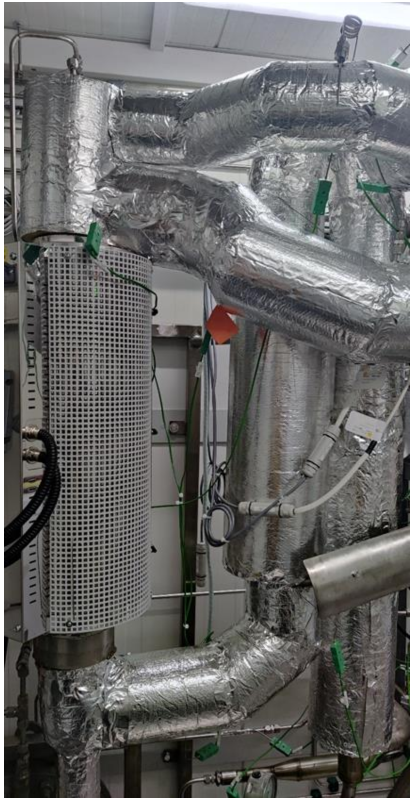
Catalytic partial oxidation (CPOx) coupled with rWGS



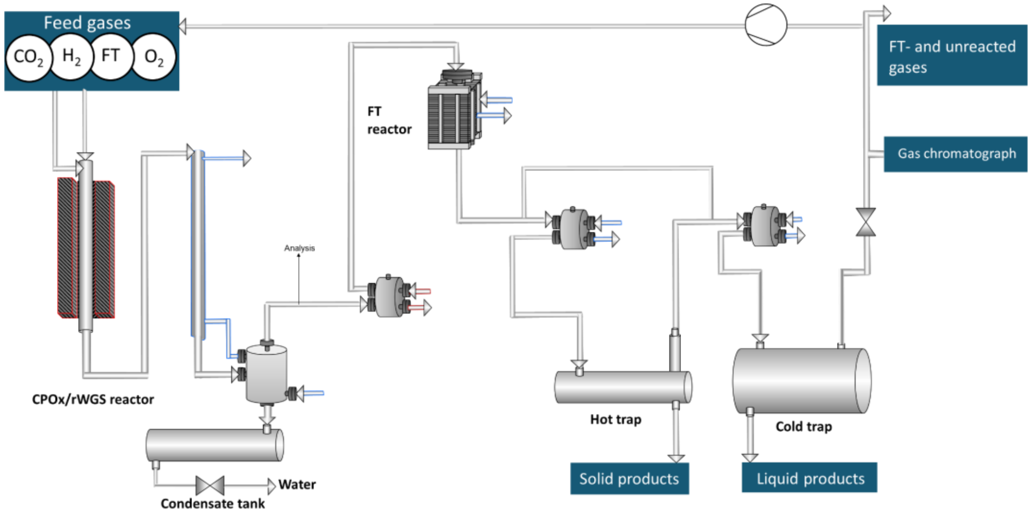
- Successful first tests realised in Decarbonate project, TRL5
- Oxygen feeding controls carbon formation in rWGS.
  - Improved feed versatility: FT off-gases can be more effectively re-circulated
- In-situ heat production with more uniform temperatures and fast control

$CO_2 + H_2 \rightleftharpoons CO + H_2O$ ΔH° = 42 kJ/mol

$H_2 + 0.5O_2 \rightleftharpoons H_2O$ ΔH° = −286 kJ/mol



Mobile synthesis unit (MOBSU)



- MOBSU CPOx/rWGS process at TRL ~4
  - Precious metal catalyst and high throughput tubular reactor configuration
  - Coupled to downstream FT synthesis (Ineratec)

CPOx/rWGS with FT recirculation

- Tested for short periods with a recycle rate of ca. 50% of FT off-gases (and 50-60% CO conversion at FT)

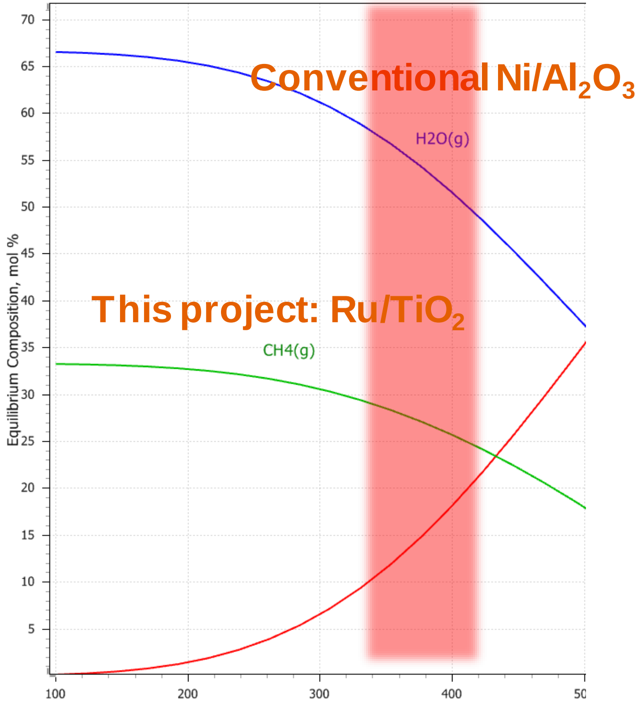
- Initial results positive – predicted CO_2 utilisation increase
  - Full or almost full conversion of C2-C5 FT species according to gas GC results

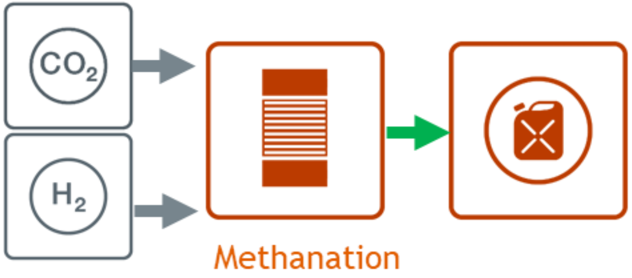
- Carbon formation the biggest question mark
  - Positive results, but current tests (6-12 h) with FT recirculation too short to draw conclusions

Methanation by the Sabatier reaction

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$

$\Delta H_{278K} = -165{,}1\ \mathrm{kJ/mol}$





- Very exothermic and rapid reaction
- Good heat control essential
- Lower operating temperature beneficial

Methanation connected to a calcination kiln (VTT Tampere)

- Lab scale methanation reactor connected to the outlet of a calcination oven
- Slipstream flow 1 – 2 ln/min CO_2
- Oil cooled HEX-reactor
- Activated carbon gas cleaning
- Can be operated by daily basis
- Test runs realised in March 2021 at VTT Tampere

Reactor tube

Methanation test unit ”MoMe”

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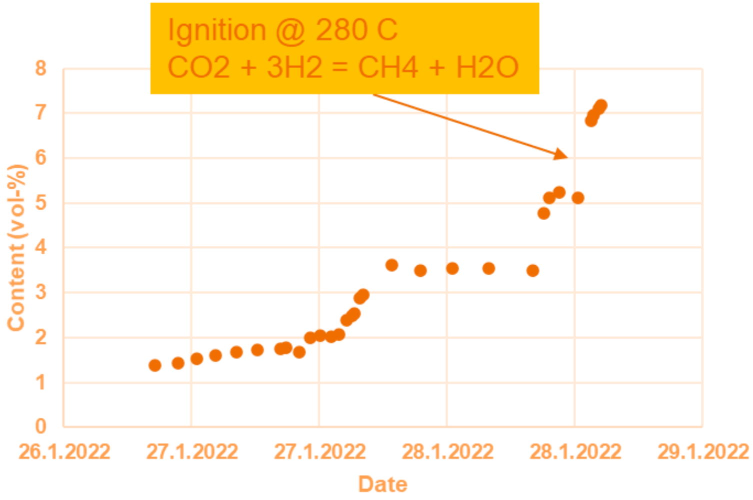
Methanation

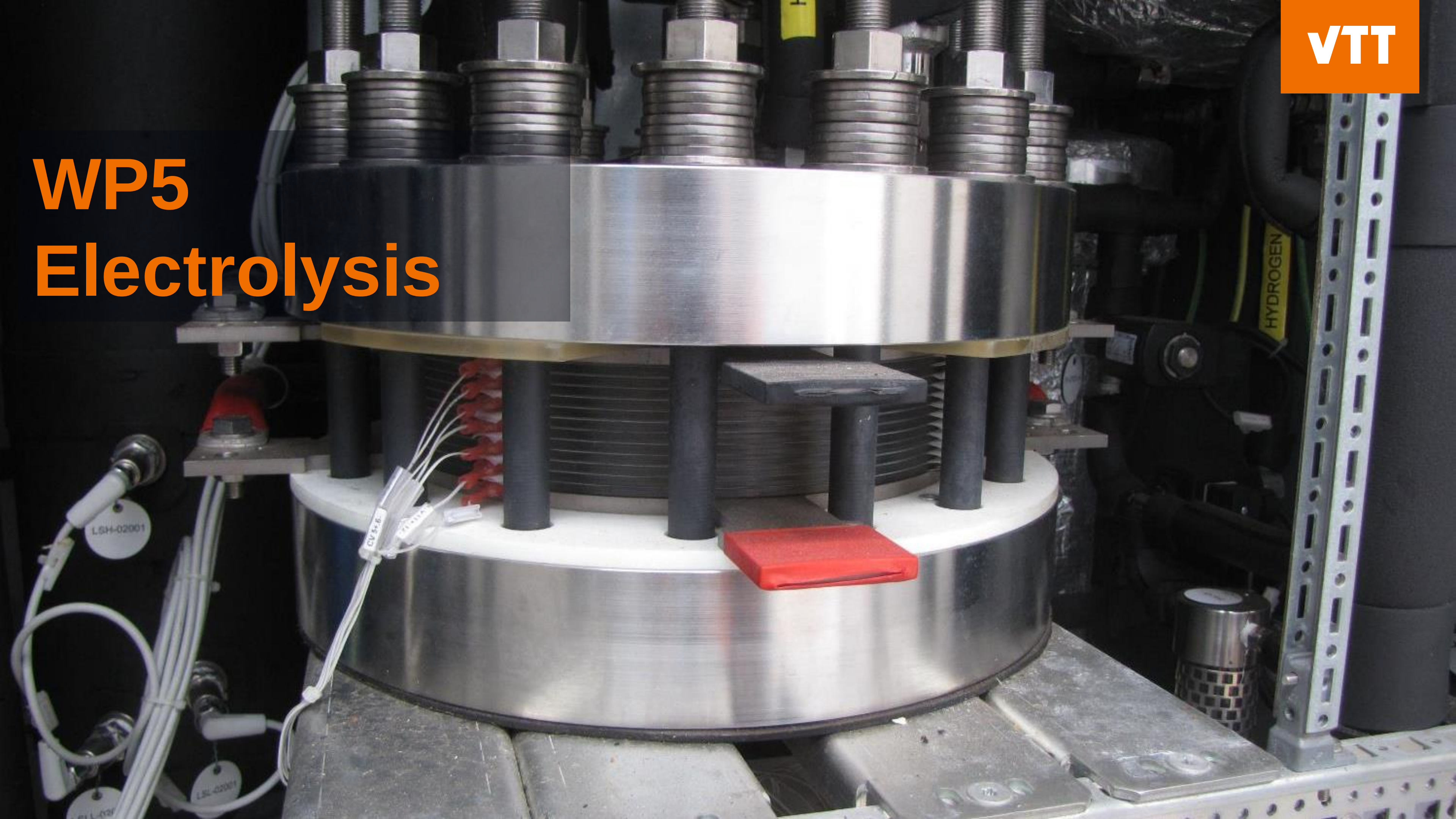
- Direct CO_2 methanation
  $CO_2 + 3H_2 = CH_4 + H_2O$
- Two concepts for the methanation reactor:
  - Packed bed tube heat exchanger
  - “Millichannel” heat exchanger
- Test runs realized at VTT Tampere (packed bed) and at Otaniemi lab (millichannel)
- Ru/TiO_2 catalyst active at higher Ru-load
- PoC tests succesfull for the millichannel reactor, TRL3



WP4 Conclusions

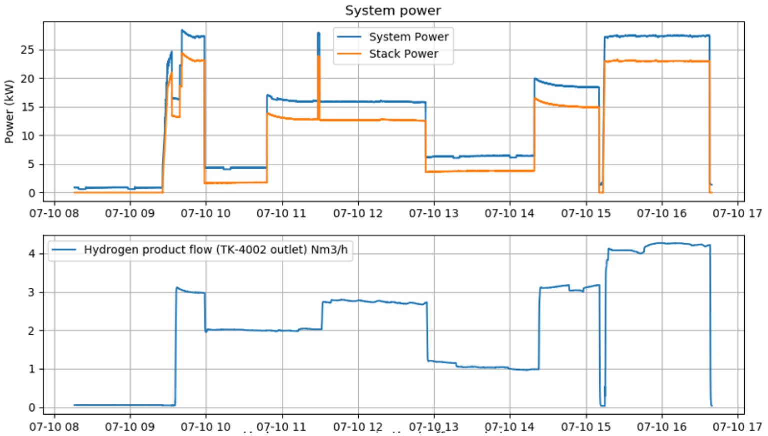
- CO_2 conversion to syngas by CPOx/rWGS successfully demonstrated at TRL5
- FT off-gas recycling and efficient utilization of CO_2 demonstrated at TRL5
- Methanation concept utilizing heat exchanger reactor and Ru/TiO_2 catalyst proofed at TRL3

WP5
Electrolysis



Development of dynamic operation model

- First test operations were performed with a small scale PEM electrolyser (30 kW_{el})
  - Operation data was used to study process behaviour and find limitations for operation
- Simulation model to optimize larger scale electrolysis operation was built
  - Parameters for larger scale operation was gathered from commercial systems
  - Electricity prices were imported from Nordpool, grid service compensations from Fingrid and other costs were estimated based on literature sources



Scenarios for model

- Optimized operation was compared to the stable hydrogen production in different real and manipulated electricity market conditions
- Electrolysis capacity of 9 MW_{el} was selected for optimized operation corresponding to current large scale PEM electrolyser systems
- Load range for dynamic system was selected to be 10 – 100% and no shut downs were allowed to ensure fast response times

Optimum is only valid for the chosen set of parameters and assumptions!

Electricity market scenarios:

- FI 2018 Spot
- FI 2019 Spot
- Volatility changes 120, 200 %
- (no tax or transfer cost added)

Parameter	Optimized operation	Stable operation	Unit
Electrolysis Capacity	9 000	7 200	kWel
Nominal H_2 production	2000	1600	Nm^3/h
Nominal efficiency	78	78	% (HHV)
Load range	10 – 100	100	%
CAPEX*	1000	1000	€ / kWel
Annual fixed OPEX	5	5	% of CAPEX
Storage capacity	24	24	Hours of nominal production
H_2 consumption	80	100	% of nominal production

* APR: 8 %, terms: 20

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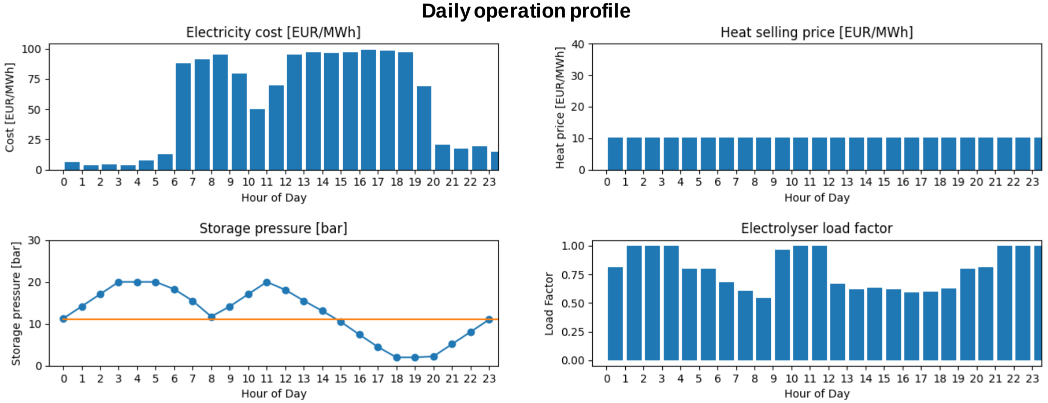
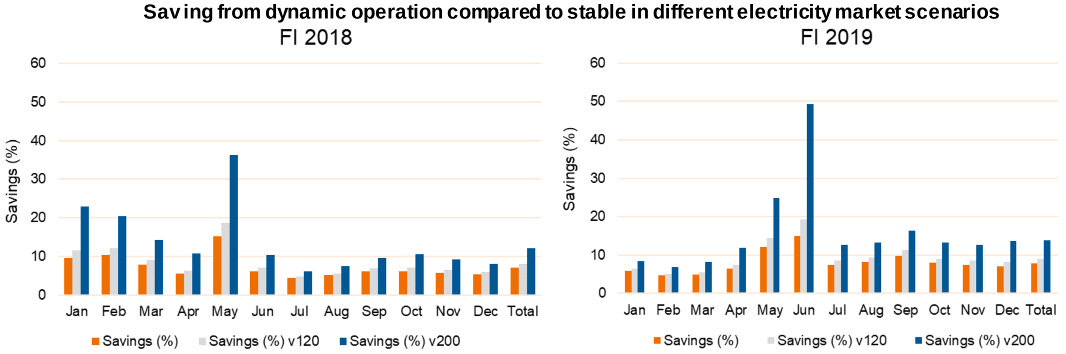
Main results

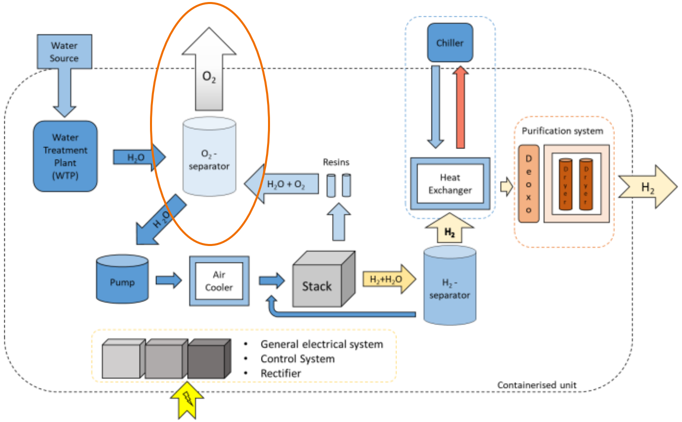
- Electricity price volatility and hydrogen storage capacity enable savings by dynamic operation compared to stable production
- Optimization limitations/boundaries
  - Electricity cost future data
  - Hydrogen storage capacity
  - Hydrogen consumption (user need)
  - Electrolysis system operation range including overload capability
  - The system efficiency
- Increasing electricity price volatility and decreasing system CAPEX make dynamic operation more profitable
- Grid services can offer additional revenue for electrolyser operator if system capacity is sufficient for TSO's requirements





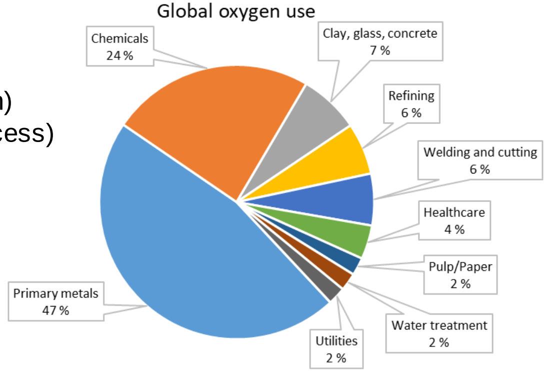
Oxygen utilisation

The by-product O_2 from the stack contains water and possibly small amounts of H_2. Therefore, the purity of the oxygen gas depends on drying and purification processes after the stack. The product O_2 gas quality after drying process is typically in range of 99 – 99.8% for AEL and even higher for PEM [1,2,3]



1 Buttler et al. 2018
2 Iora et al. 2009
3 Albrecht et al. 2017
4 BBC Research, 2018

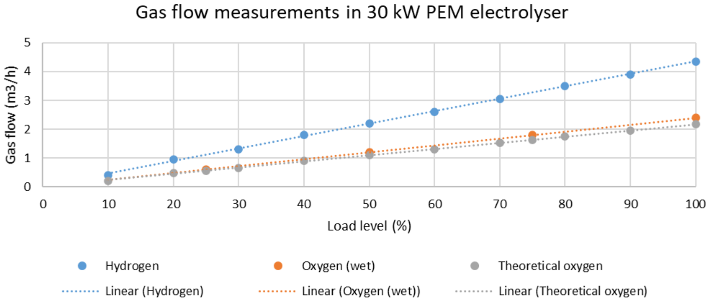
Global oxygen market includes many applications in chemical industry, glass manufacturing and medical use[4]



Oxygen utilization in Power-to-X projects:

- Green H2F Puertollano I (nitric acid production)
- Westküste 100 (cement plant combustion process)
- P2X Solutions (nearby industrial processes)
- Hychico (sold to oxygen market)
- Myrte (Utilized in fuel cells)
- Wunsiedel (nearby industrial processes)

8 kg of O_2 is produced for every 1 kg of H_2: $H_2O_{(l)} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}$



Oxygen utilisation cost estimations

- Delivered O_2 price from suppliers depends on
  - O_2 supply amounts and quality (gas pressure/liquid)
  - Fees for storage equipment (tank, evaporator, etc.)
  - Transportation cost (distance and frequency)
- Other remarks
  - Liquid oxygen boil-off (2 – 5 %/d of total mass)

Oxygen price ranges	
Liquid, industrial scale	45 – 480 €/tn [1,2,3]
Gas, bottle (> 99.5 % purity)	1000 – 3500* €/tn [3,4]

* Even higher with > 99.995 % purities

1 StatFin 2020
2 ACEEE 2007
3 VTT Internal
4 Nicita et al. 2020

O_2 treatment and storage cost estimations[1]

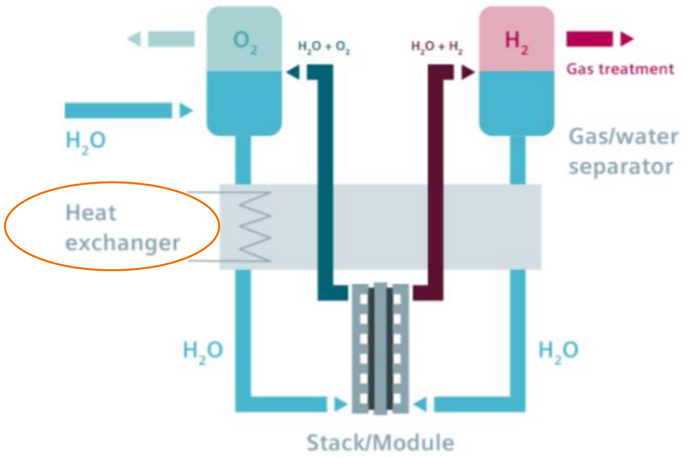
Electrolysis > 1 MW → Dryer 180 – 264 k€ / Compressor 80 – 131 k€ → Storage 100 m³ 170 – 220 k€ → Transportation

Leading to 100 – 150 €/tn cost

[1] Gretzschel et al. 2020

Waste heat utilisation

- Waste heat can be extracted from the electrolysis at around 50 – 70 °C temperature
  - Higher temperatures can be achieved with the aid of heat pump
- Depending on electrolyser system design, the estimated heat recovery can be 15 – 25 % of power input
- Large scale application for the waste heat is district-heating network
  - Price for the heat typically depends on heat delivery temperature and ambient temperature of the network area



Siemens

WP6 Business opportunities

CO_2 market outlook

USA

- Oversupply of CO_2 in the Midwest, most CO_2 sources outside of the Midwest are tapped
- Potential areas include California, Texas and Northeastern U.S.

Europe

- Largest market for CO_2 in United Kingdom, Netherlands, France, Poland and Germany
- High number of ammonia and ethanol production plants across Central and South Europe
- Lime production increasing in certain Central and Eastern European countries
- Supply shortages indicate that new CO_2 sources in Europe are needed, especially if ammonia production will turn to electrolytic hydrogen

China

- Cement production decreasing but pulp and lime production increasing
- Most potential areas for low-cost RE production and population centers have different locations
- Adequate transmissions capacity can bring low-cost RE where it is most needed and RE does not need to be produced locally

Matching CO_2 supply and demand is challenging due to geography and seasonality of supply
→ CO_2 market study on local level and local value chain creation are important

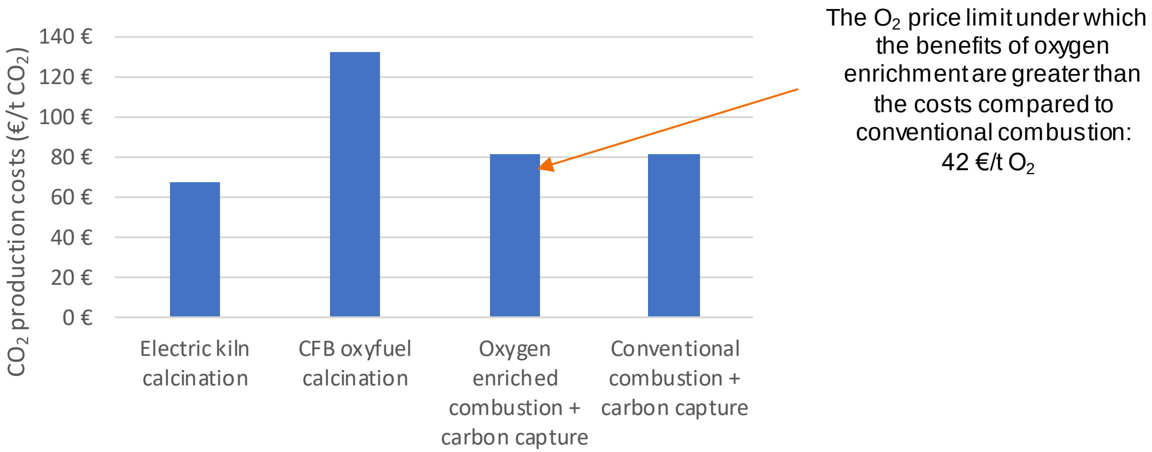
Link to the publication: https://www.decarbonate.fi/wp-content/uploads/2020/12/Decarbonate_CO2_webinar_June_2020.pdf

Techno-economic comparison of CO_2 capture concepts

- Only costs differing from the reference calcination process are allocated to CO_2
  - The reference calciner has same costs for labor and $CaCO_3$, and the same revenue related to production of CaO
  - → Labor, $CaCO_3$ and CaO are excluded from the economic assessment (fuel is included in electric kiln calcination case as savings)
- Prices used in calculations: Purchased O_2 40 €/t, electricity 40 €/MWh

	Calcination concepts		Power plant concepts	
	Electric kiln calcination	CFB oxyfuel calcination	O_2 enriched combustion + carbon capture	Conventional combustion + carbon capture
Amount of captured CO_2 [kt/a]	74 (+ 41 avoided)	110	814	814
Investments for CO_2 capture [M€]	61	63	185	202
Investments include	• Calciner • Simple CO_2 purification	• Calciner • Flue gas recycling equipment • Simple CO_2 purification	• CO_2 capture and purification unit • O_2 storage	• CO_2 capture and purification unit
Capacity	320 t lime/day	320 t lime/day	300 MW	300 MW

Techno-economic comparison of CO_2 capture concepts



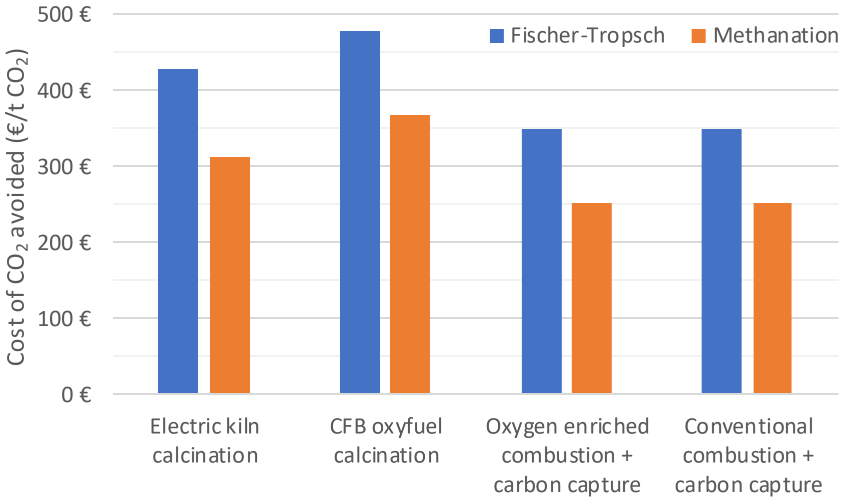
- The results are very sensitive for several uncertain parameters
  - Electricity price has biggest impact
  - Other major factors are investments and allocation of costs between CO_2 and other products

→ Volatility of electricity price increases uncertainty significantly. On the other hand, participation in the reserve markets can offer additional revenue and improve feasibility of the concepts

Techno-economic comparison of concepts integrated with synthesis

- Alkaline electrolysis for H_2 production for methanation and FT synthesis
- O_2 from electrolysis utilized onsite in oxyfuel and oxygen enrichment cases, excess O_2 sold to market
- Investments added to previous concepts (table):

	Investments [M€]	Calcination concepts		Power plant concepts	
		Electric kiln calcination	CFB oxyfuel calcination	O_2 enriched combustion + carbon capture	Conventional combustion + carbon capture
Fischer-Tropsch	Electrolyzer	52	86	591	576
	FT units	58	76	290	290
Methanation	Electrolyzer	60	98	674	660
	Methanation unit	47	61	232	232



WP7 Dissemination and international collaboration

Yle Central Finland and Yle Southern Savonia. TV News, Oct 12th, 2021.

WP7 – Examples of communication activities

VTT

LIVE virtual presentation of the electric rotary kiln to 100 participants by Oona Katajisto, VTT.

Key messages on video **in Youtube:** https://youtu.be/3YhQwnl6qAY

Virtual opening ceremony on Oct 12th, 2021, keynote speaker **Krista Mikkonen, Minister of the Environment and Climate Change.**

Yle News – Central Finland and Southern Savonia. **TV news** and **hourly news on the radio** on Oct 12th 2021.

KESKISUOMALAINEN

Keskiviikkona 13.10.2021

Sementin päästöt pois

VTT: Jyväskylässä on kehitetty teknologiaa, joka voi mahdollistaa hiilidioksidipäästöttömän sementtitehtaan. Hankkeen keskiössä on sähkökuumenteinen rumpu-uuni. Sivut 14-15

Front page headline in the magazine Keskisuomalainen on Oct 13th, 2021.

Harppaus kohti päästötöntä betonia – VTT kehitti 1000-asteisen kaasutiivin sähköuunin sementin valmistukseen

Example article from the Tekniikka & Talous –magazine.

...a total of 20 news & occupational magazine articles!

DE CARBONATE

VTT

WP7 International collaboration

14 conferences, workshops, seminars and webinars with IEA, TEM, CO_2 Value Europe, Global CemPower Conference & Exhibition, TEK, The national congress on air pollution prevention and climate issues (Ilmansuojelupäivät), Annual Global Innovative Catalysis Development Forum, DERlab and others

+ meetings with international stakeholders, e.g. the British Embassy in Finland, the Finnish Embassy in Thailand and international companies!

4 scientific articles in preparation:

- Experimental study on decarbonazing cement production by oxyfuel combustion, **Pikkarainen et al.**
- Oxygen-enriched CFB combustion with carbon capture from flue gas, **Leino et al.**
- Comparison of CO2 capture and utilization concepts enabled by cheap and volatile renewable electricity, **Winberg et al.**
- Benefits of hydrogen enrichment on indirectly heated calcination of CaCO3 - Results of lab scale experiments with rotary kiln, **Katajisto et al.**

DECARBONATE

VTT

beyond the obvious

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