KOMMERZIALISIERUNG VON SAUERSTOFF-GENERATOREN AUF BASIS GEMISCHT LEITENDER MEMBRANEN

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State: 10/2023

OUTLINE

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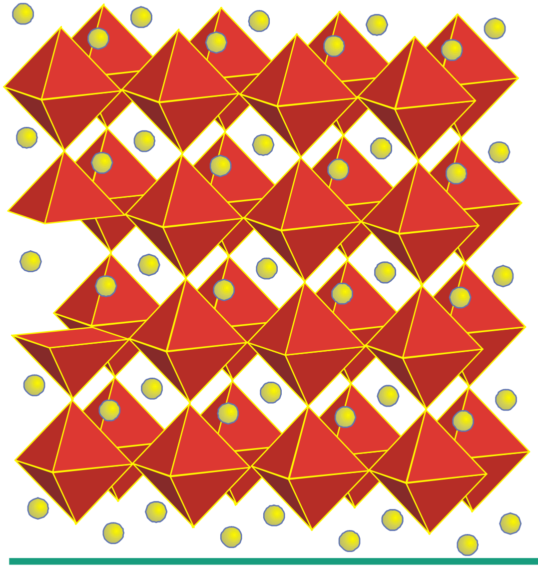
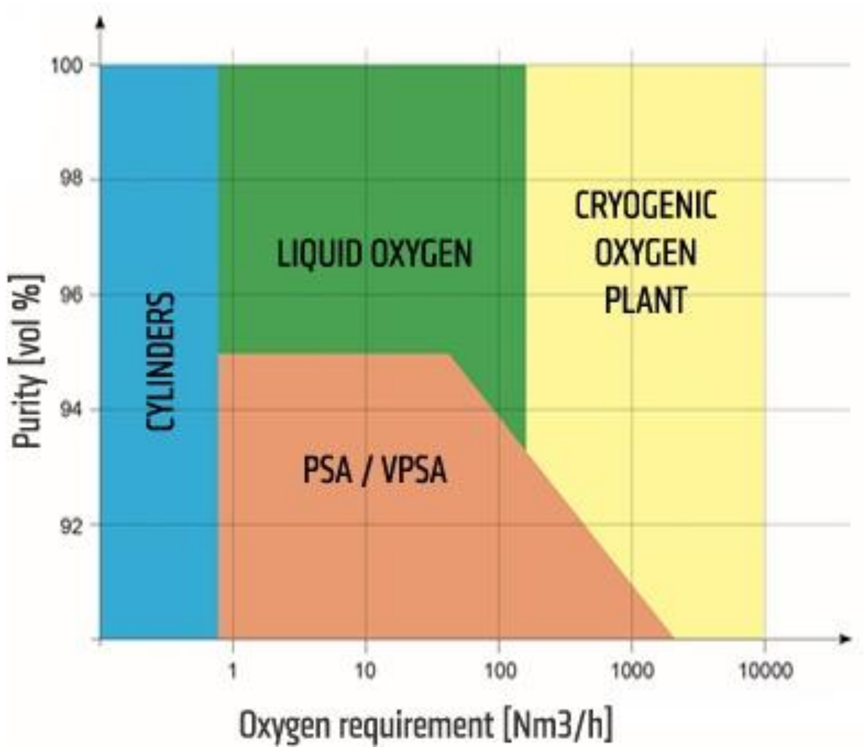
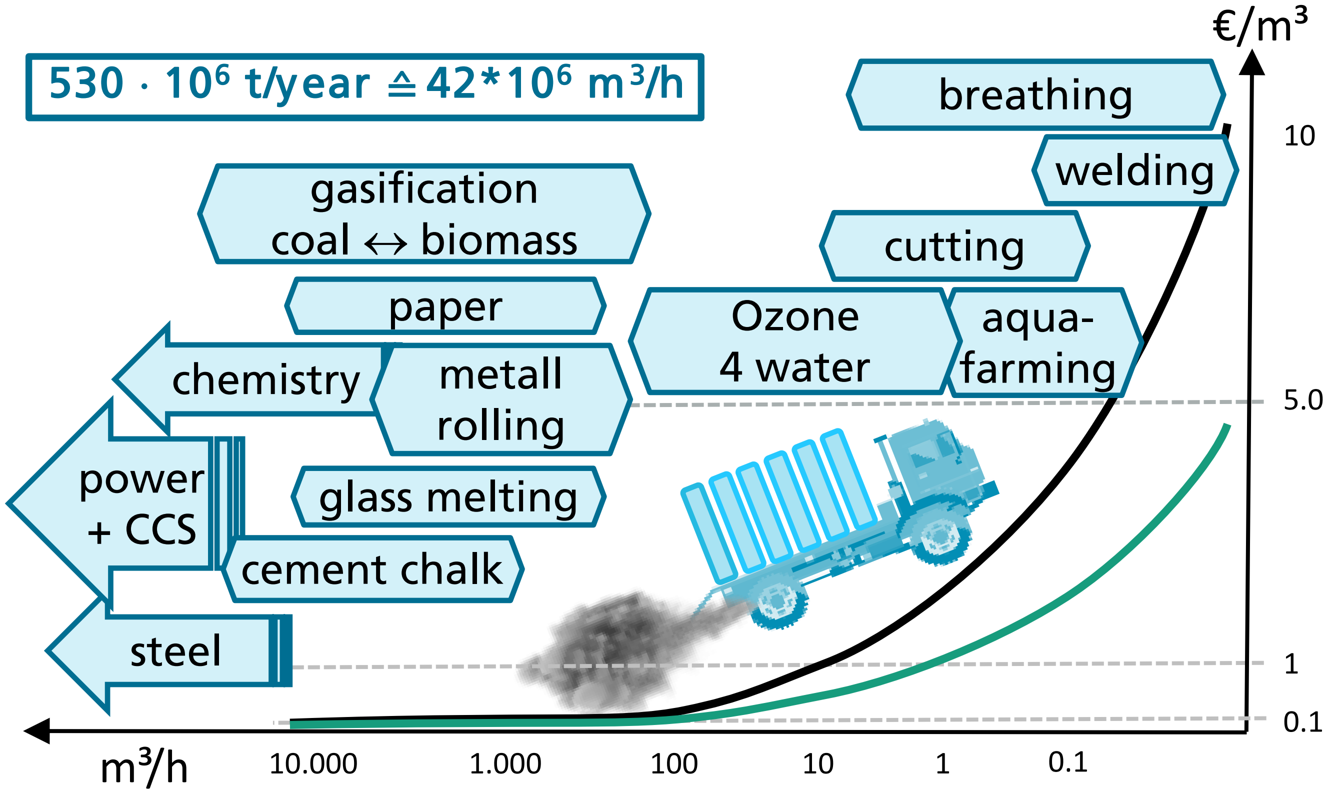


Achema, 05/2009

Introduction:

Oxgen: Comparison of Production Technologies





global market size: **~34 billion €/year**

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MIEC (Mixed Ionic Electronic Conductor) Membranes:

How it works …

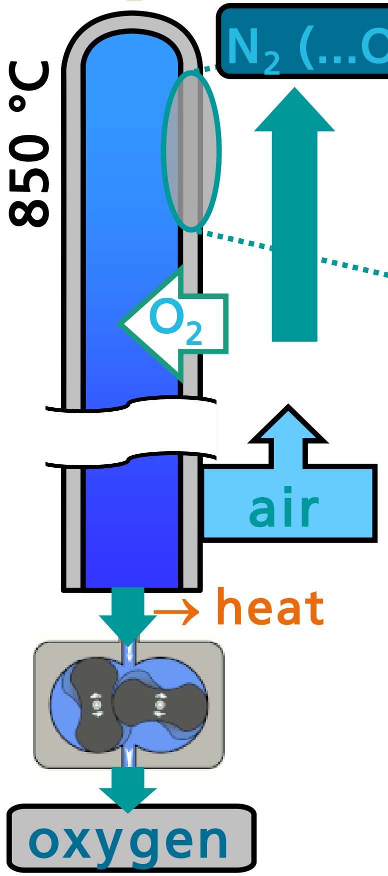
→ O. Ravkina: 14:45 im Ford-Saal

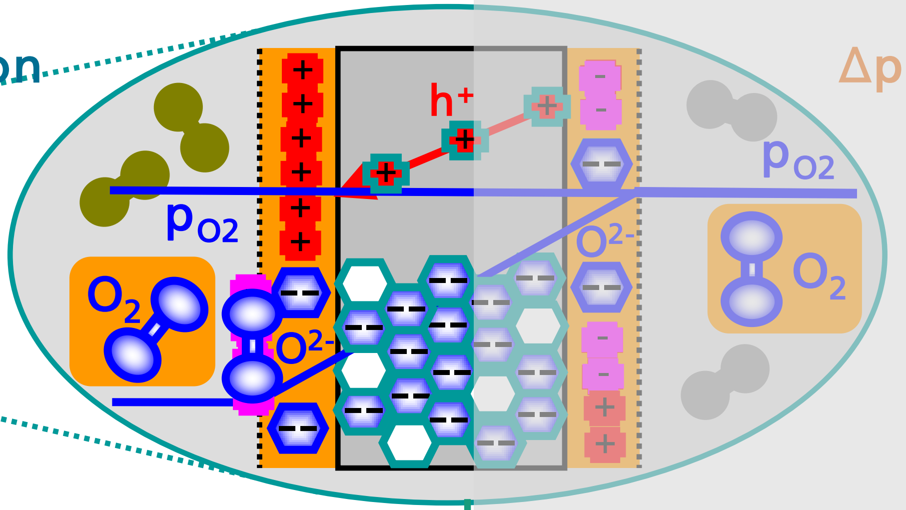
Membrane Separator

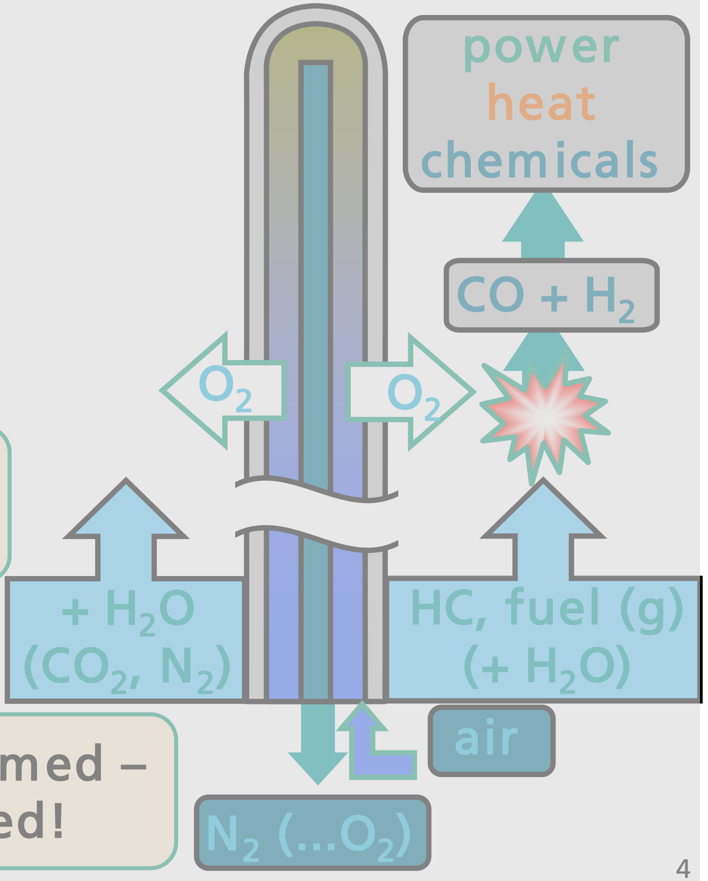
$\Delta p(O_2)$ by gas compression

Membrane Reactor

$\Delta p(O_2)$ by an O_2 consuming reaction







indirectly heated by a thermal process

(needs energy)

directly heated by reaction enthalpy

(delivers energy)

driven by $\Delta p(O_2)$

needs power for generation of $\Delta p(O_2)$

$\Delta p(O_2)$ by O_2 consumed – no power needed!

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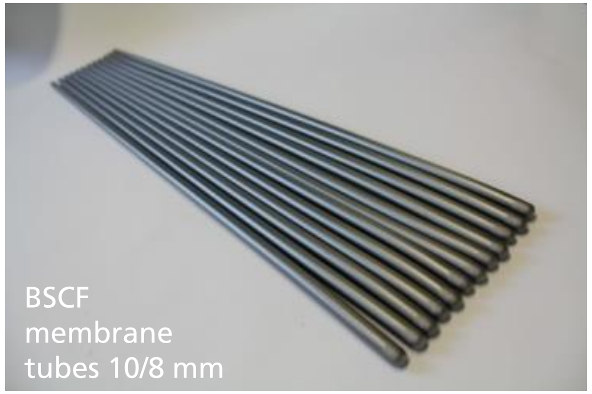
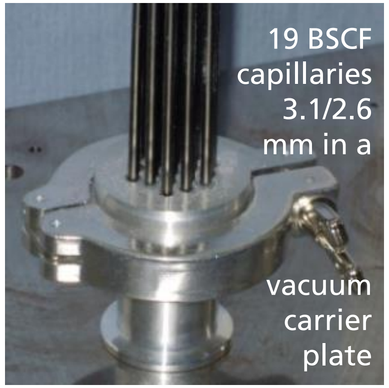
MIEC Membranes:
Performance for O_2 Production



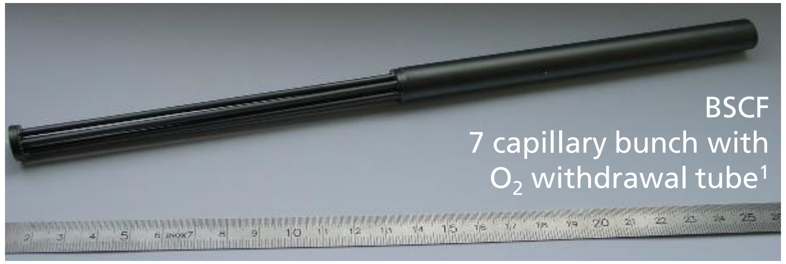


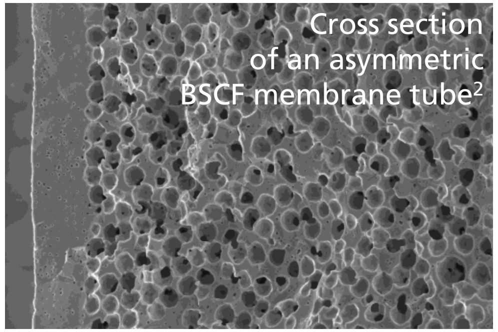
State of the art (@ Fraunhofer IKTS):

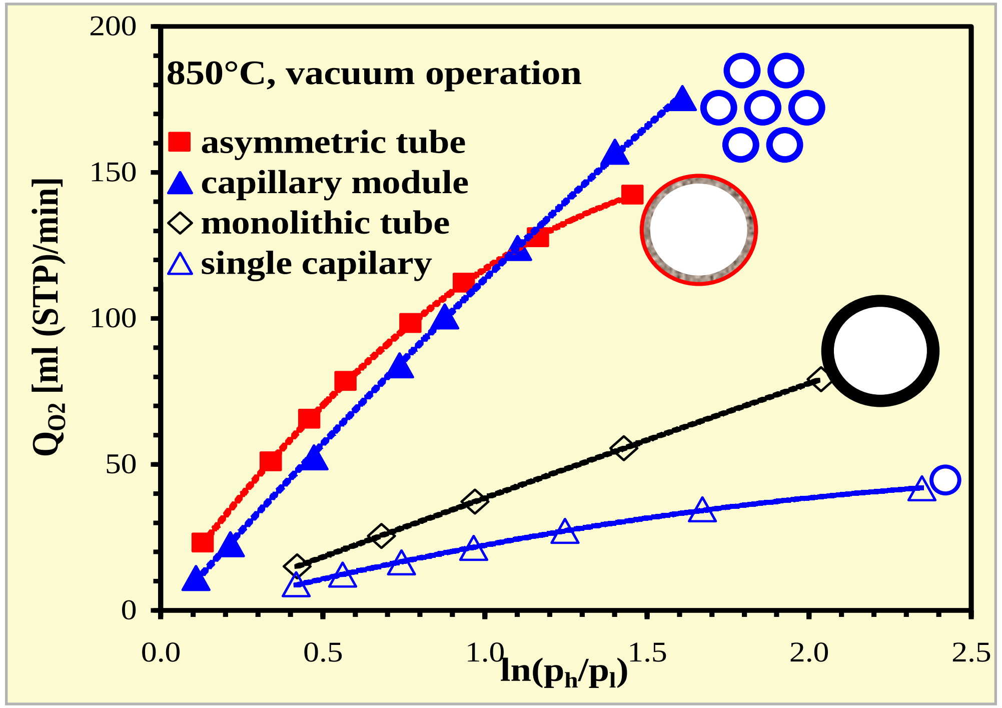
- stiff-plastic extrusion: monolithic tubes, capillaries
- C: high **shock tolerance, cheap** at mass production

R&D: Advanced membranes:

- higher O_2 flux and packaging density
- **asymmetric:** thin separation layer on porous support
- **multichannel** tubes and **capillary bunches**
- combinations thereof







[1] Schulz, M., Pippardt, U., Kiesel, L., Ritter, K., Kriegel, R., AIChE J. 58 (2012) 10, 3195 – 3202; [2] Pippardt, U., Böer, J., Kiesel, L., Kircheisen, R., Kriegel, R., Voigt, I.: AIChE J. 60 (2014) 1, 15 - 21

Oxygen Membrane Plants:
Oxygen Generator Prototypes by IKTS

0.17 m³/h
10 kWh/m³
2009

0.35 m³/h
6 kWh/m³
2011

1.5 m³/h
1.6 kWh/m³
2013

Tubes Ø 10 mm & Recuperative Heat Exchanger

1st proof of concept — Long-term stability — Industrial feasibility

RTM

0.22 m³/h
4 kWh/m³
2015

1 m³/h
1.6 kWh/m³
2015

10 m³/h
0.72 kWh/m³
2017

Capillaries Ø 3 mm & Regenerative Heat Exchanger

Portable Demonstrator — Pilot plant — Energy efficiency

Air Liquide — **MedPROmM**

Research Award Thuringia 2010

- Tubes 7,500 h
- Caps 18,000 h
- still running

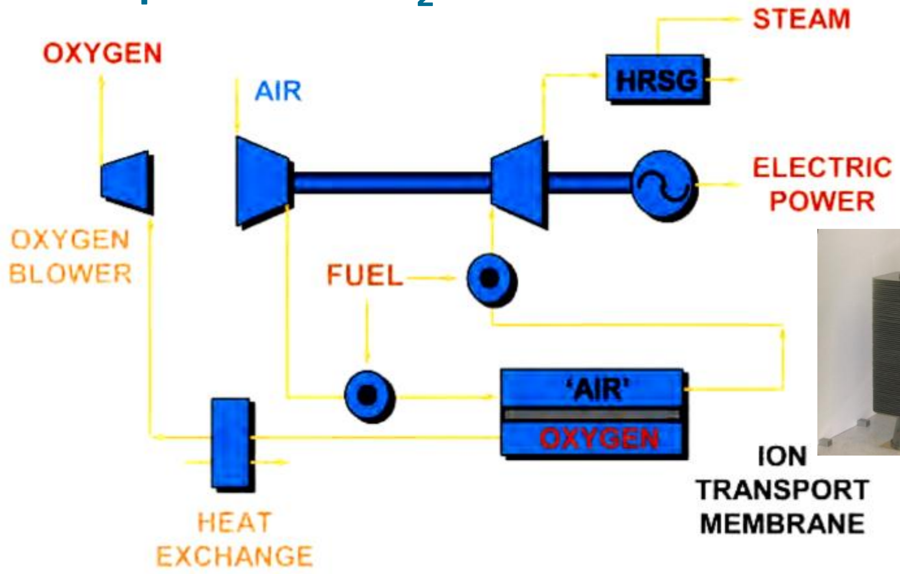
cryogen >0.46 kWh/m³
MIEC: 0.2 kWh(el.)/m³ + 0.25 kWh(therm.)/m³

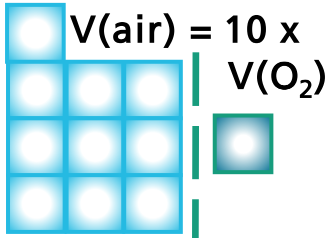
USP: Patented Vacuum Operation Route - Continuous Improvement

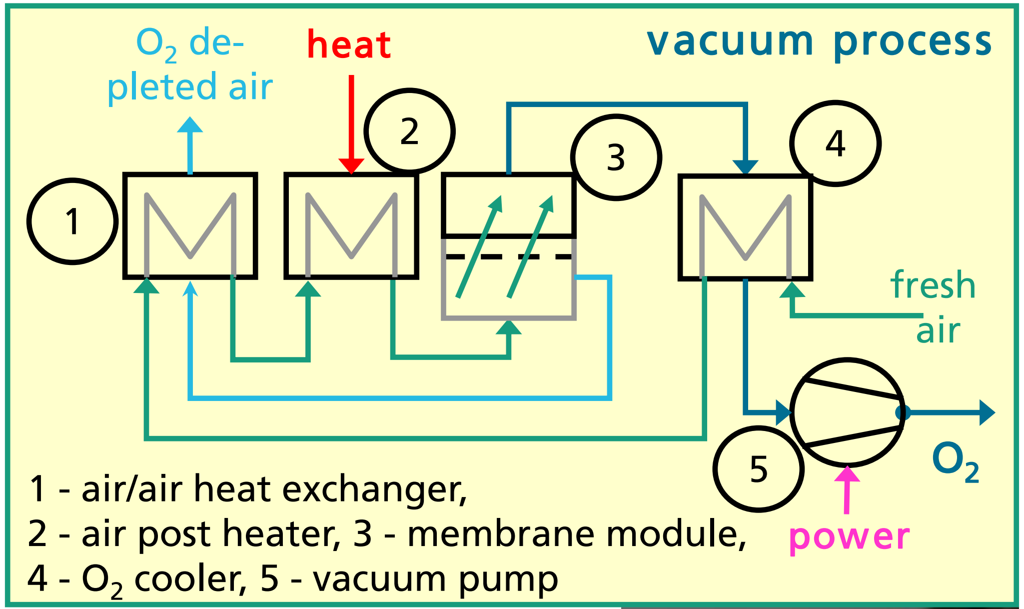
Oxygen Membrane Plants:
Overpressure vs. Vacuum for O_2 Production

Expert opinion: A stand-alone MIEC plant producing O_2 only is not competitive!

Overpressure: O_2 + Power







Air Products and Chemicals: O_2 + Power
expensive **pressure vessel**, very efficient turbo components, **recovery** w_{co} → large scale only
terminated in 2015 by management decision

IKTS[1]: producing O_2 only by heat exchangers & vacuum pump
→ very small to large scale ☺
unique patented solution

[1] Kriegel, R., DE102013107610A1, EP3022152B1, US9901866B2

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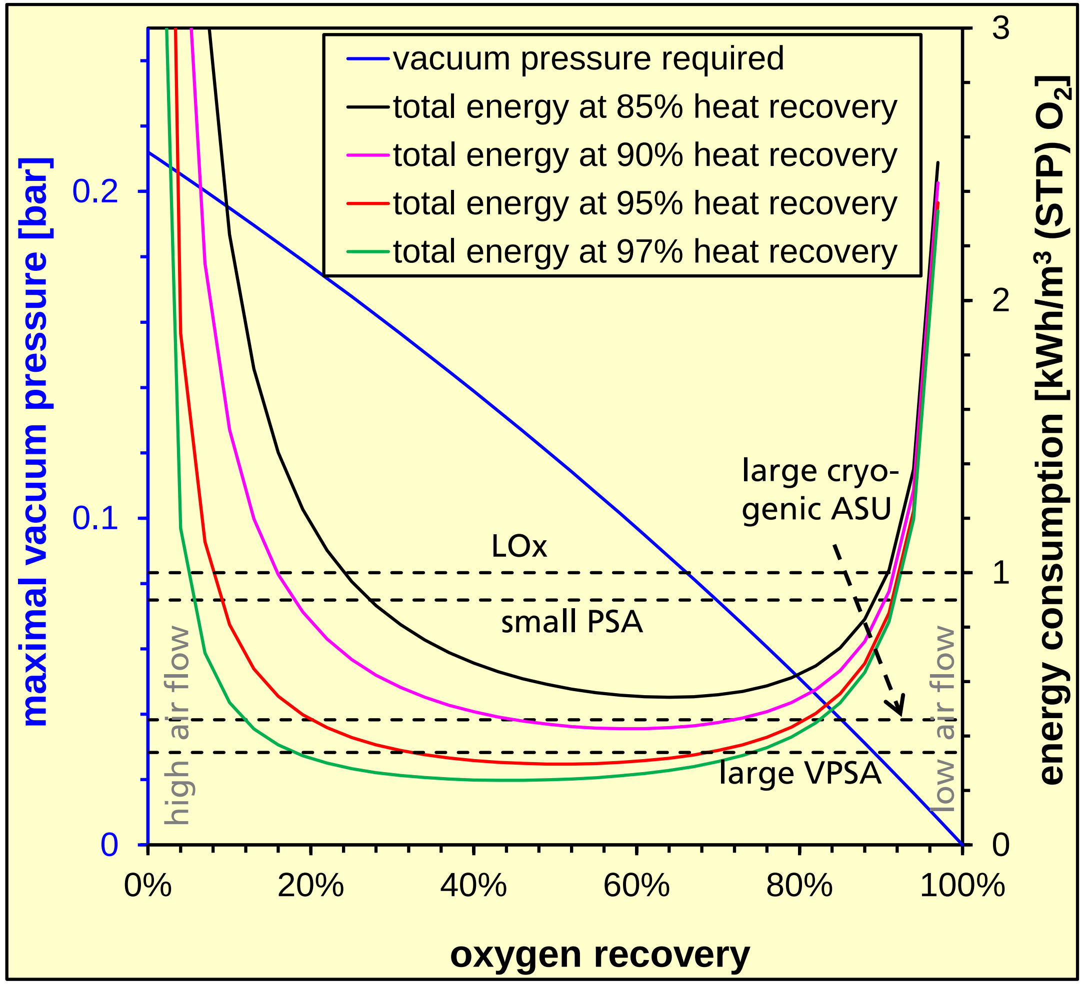
Oxygen Membrane Plants:
Total Energy Demand of Vacuum Process

Calculation of energy demand for:

- BSCF membranes @850°C, vacuum pump with 0.018 kWh/m³, varying **heat recovery**
- **energy demand caused by:**
- 1) equilibration of heat losses (~ air flux), 2) O_2 compression (~ 1/air flux)
- coupling of 1 / 2 by O_2 recovery
- **conditions for efficient operation:**
- **30 % – 70 %** O_2 recovery, **> 92% heat recovery!**
- **efficient stand-alone O_2 production**[1]
- **cost-cutting potential** by substitution of **electricity** by **gas** combustion, **waste heat**



[1] Kriegel, R., DE102013107610A1, EP3022152B1, US9901866B2

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Oxygen Membrane Plants:
OPEX: Energy Demand and CO_2 Emissions

electricity (Germany 2019): 0.10 €/kWh, 468 g CO_2/kWh[1]
natural gas combustion: 0.025 €/kWh, 202 g CO_2/kWh[2]

O_2 production process		energy demand electr.	energy demand therm.	energy costs	CO_2 total
		[$kWh_{el.}/m^3\ O_2$]		[€-Ct./$m^3\ O_2$]	[$g/m^3\ O_2$]
cryo ASU		> 0.46		4.6	215
liquid O_2		> 1.00		10.0	468
PSA		> 0.90		9.0	421
VPSA		> 0.34		3.4	159
polym membr.		> 0.35		3.5	164
MIEC membrane	el./el.	> 0.45		4.5	211
	gas/el.	> 0.20	≈ 0.25	**2.6**	144
	wh/el.	> 0.20	w.h.	**2.0**	94

Energy costs and CO_2 emissions:

- mature processes need **electricity**[1] only
- MIEC plants use also cheap **thermal energy**[2]
- transport to customer (≈70 g $CO_2/m^3\ O_2$) is not included (average distance 18.7 km/t_{gas})
- cryo ASU (= 100 %) vs. MIEC plants heated by

	energy costs	CO_2 emissions
N.G combustion	- 43 %	- 50 %
waste heat	- 56 %	- 66 %

in 2018: **competitive** regarding to **OPEX but not** for **CAPEX!**

(CAPEX ≥ 8 fold compared to PSA)

[1] Germany, 2019 (UBA): https://www.umweltbundesamt.de/publikationen/entwicklung-der-spezifischen-kohlendioxid-6; [2]AGFW FW 309-1 A2016/6 – CO_2 emissions of heat delivery.

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Competitiveness:
CAPEX Decrease by improved Membrane Manufacturing

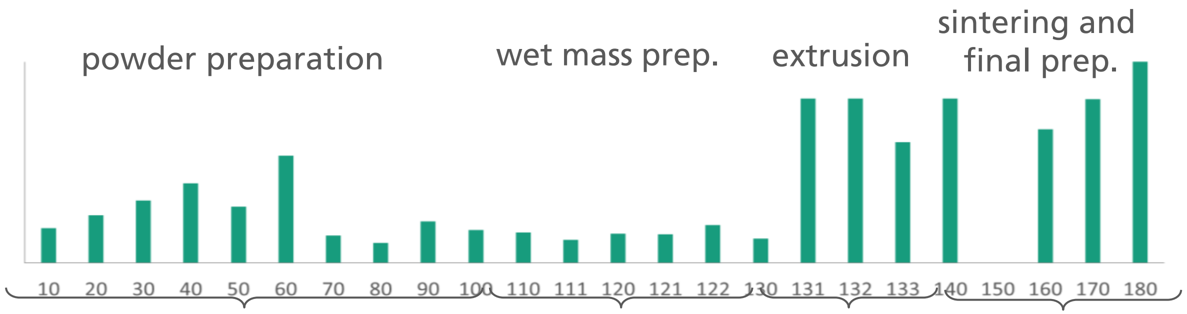
Analysis of manufacturing:

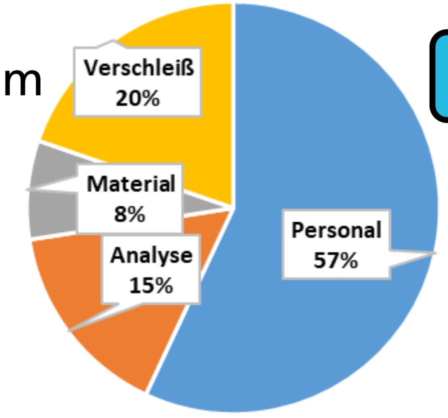
- high powder costs: **200 €/kg**
- various **expensive** work **steps**

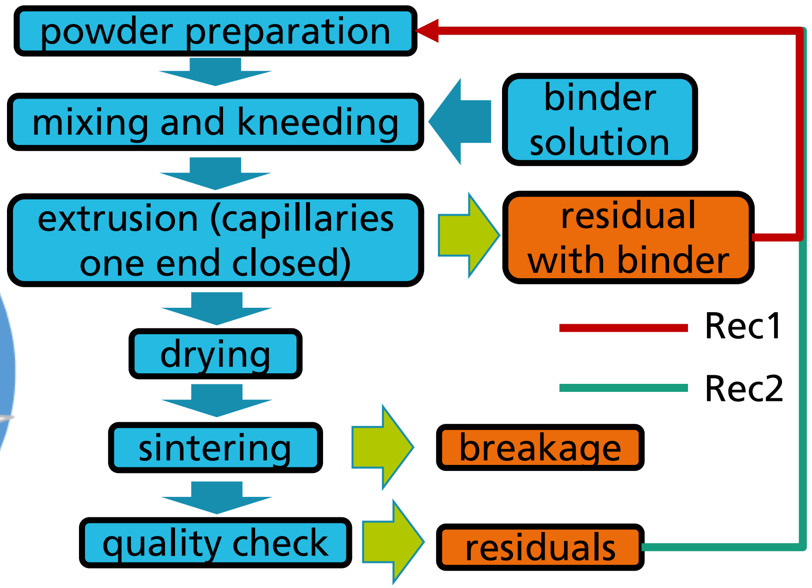
Cost decrease by:

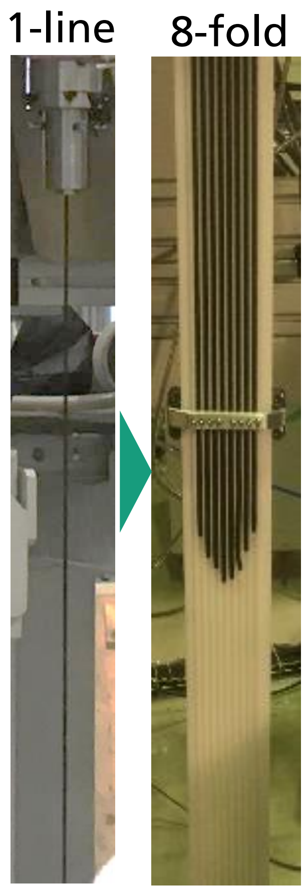
- large batch **powder preparation** for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$
- full **recycling** of all residuals
- crushing, jet milling to 2 - 3 µm
- 1-line to **8-fold extrusion**
- increase **sintering capacity**

➤ **< 100 €/kg BSCF**
< 15 €/m capillary









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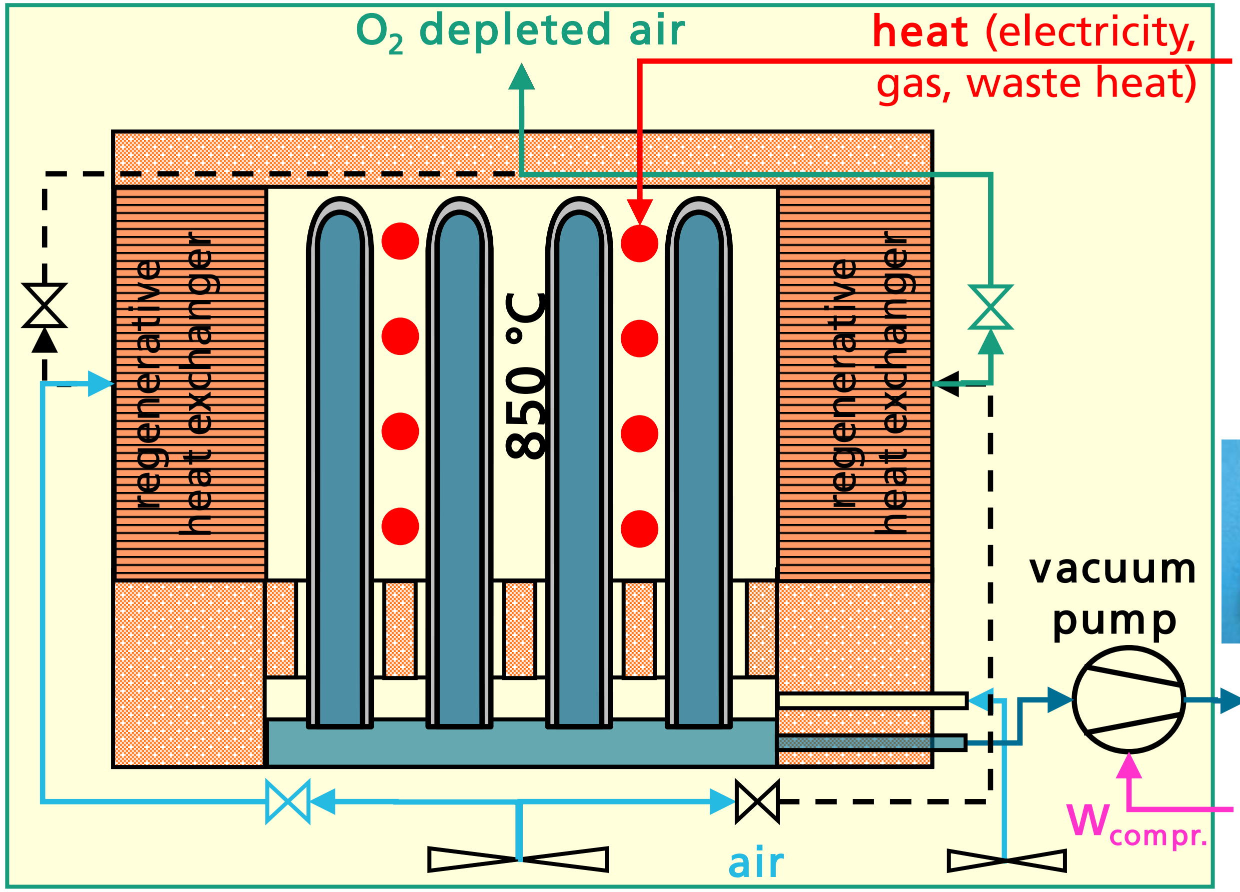
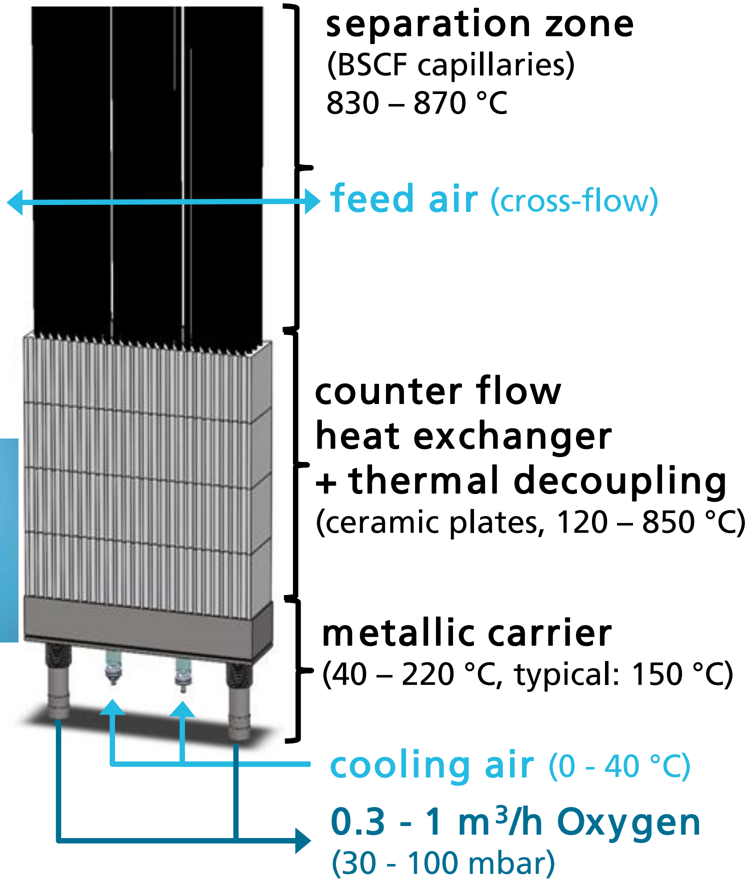
Competitiveness:
Standard Membrane Modules for simpler Mounting and lower CAPEX





SMU (2019)

[1] Kriegel, R., DE102013107610A1 (2013), EP3022152B1, US9901866B2

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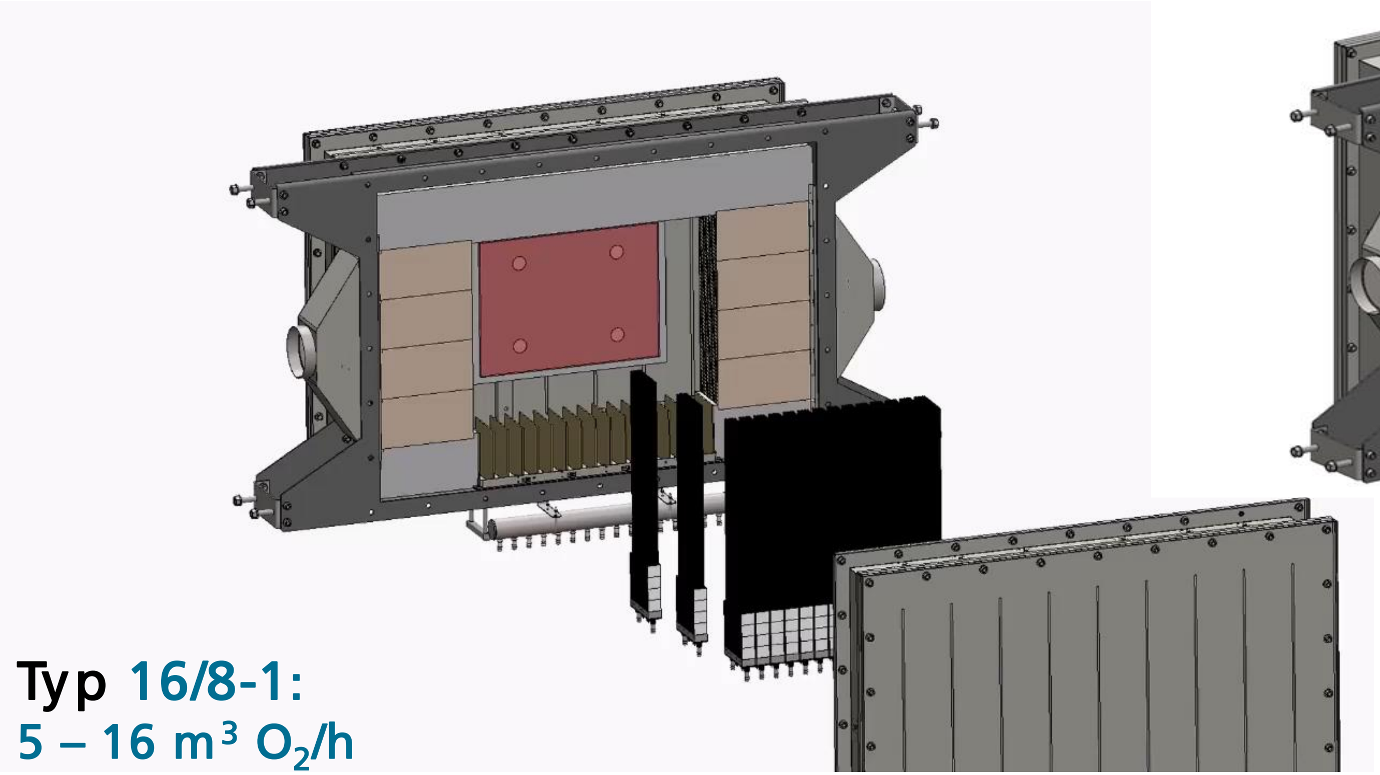
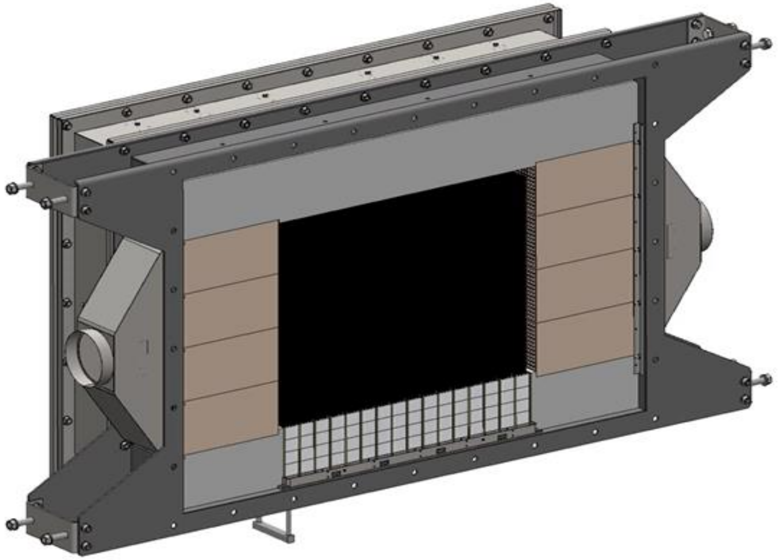
Competitiveness:
Further CAPEX decrease by improved Plant Design

- 16 **SMU** into an optimized **Frame** – arrangement of uniform **Frames** → further CAPEX decrease



Typ 16/8-1:
5 – 16 m³ O_2/h



CAPEX↓

high scalability!

Typ 16/8-5:
25 – 80 m³/h

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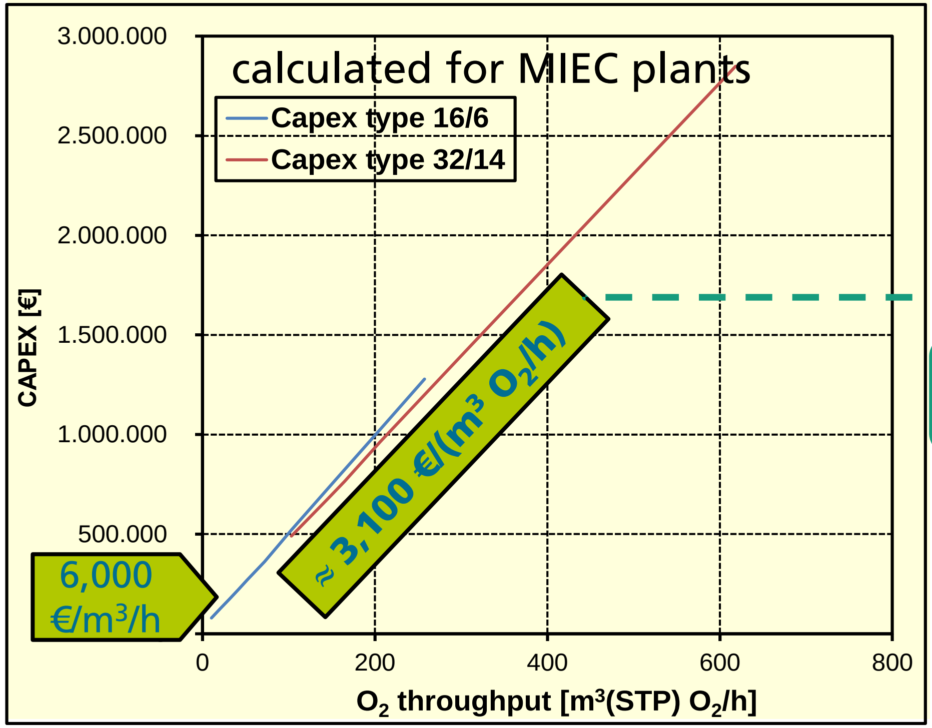
Competitiveness:
Normalized CAPEX - Comparison with mature O_2 Technologies

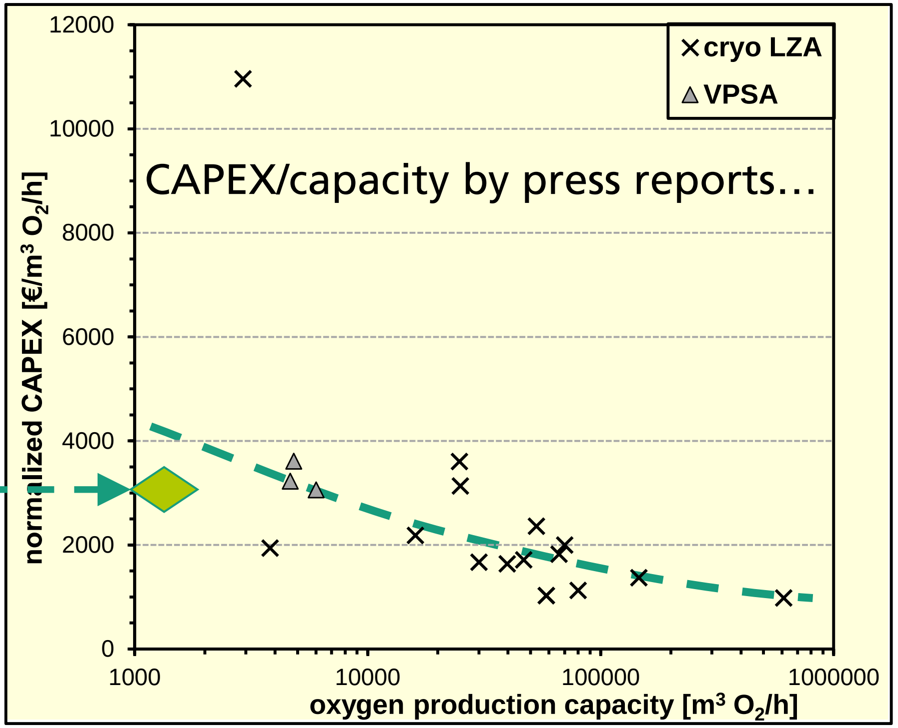
CAPEX normalized to O_2 capacity (by press reports about **cryo ASU** and **VPSA** plants)!

- **Costs:** membranes (9.50 €/pc.), SMU, casing, heater, vacuum pump, profit…



normalized **CAPEX** comparable

MIEC plant is competitive!



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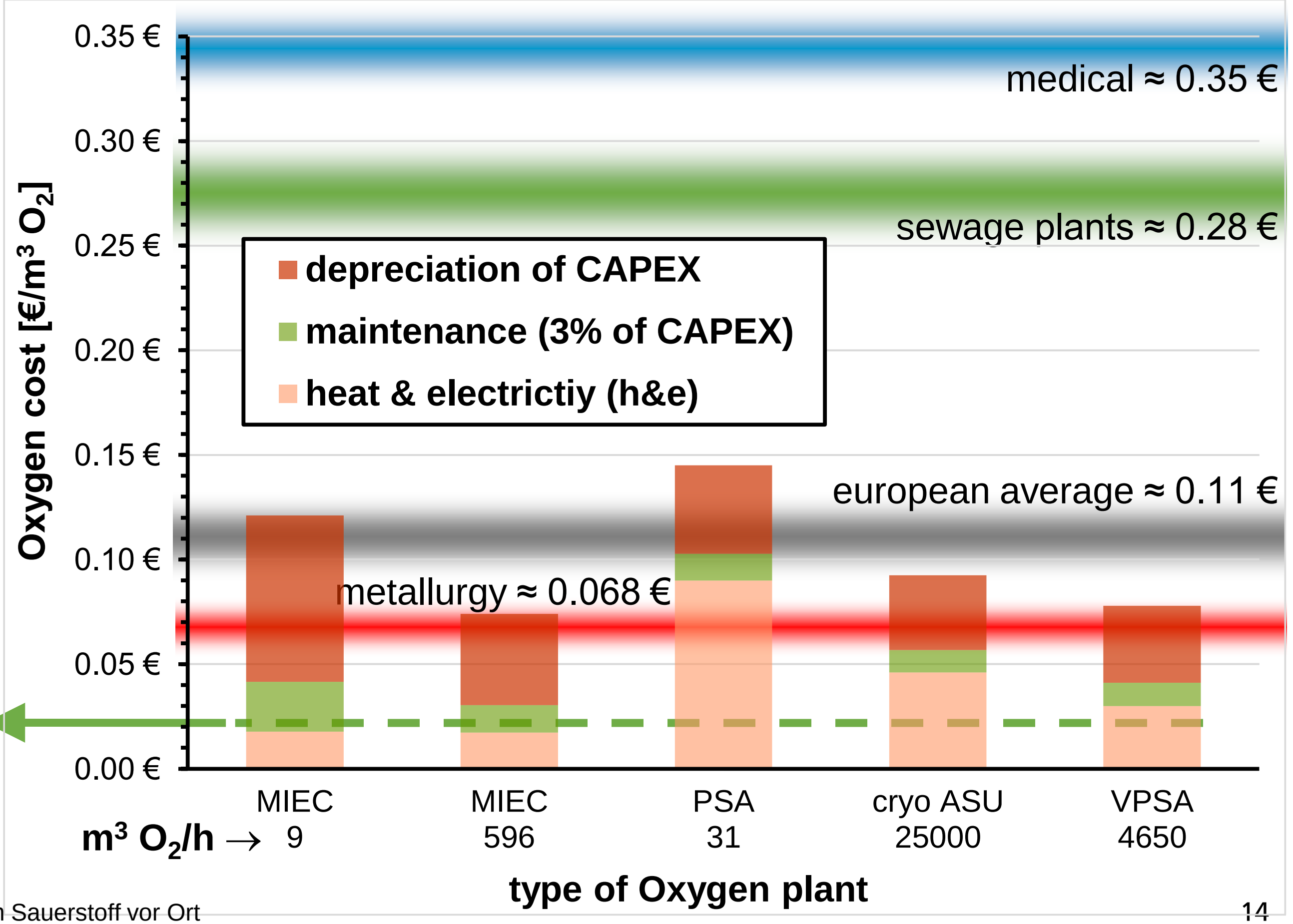
Competitiveness:
Comparison of Oxygen Production Costs

O_2 plants based on MIEC membranes:

- depreciation = CAPEX / 10 years
- maintenance = 3% * CAPEX
- h&e costs = electricity (0.1 €/kWh) + heat (0.025 €/kWh)
- 95 % annual utilization
- very low OPEX possible!
- undercutting O_2 prices @small scale

lowest energy costs and CO_2 emissions

→ poXGen[1] (04/2022, FKZ: 03EFSTH033)



[1] Kommerzialisierung der poXos® - Generatoren für die energieeffiziente Produktion von reinem Sauerstoff vor Ort

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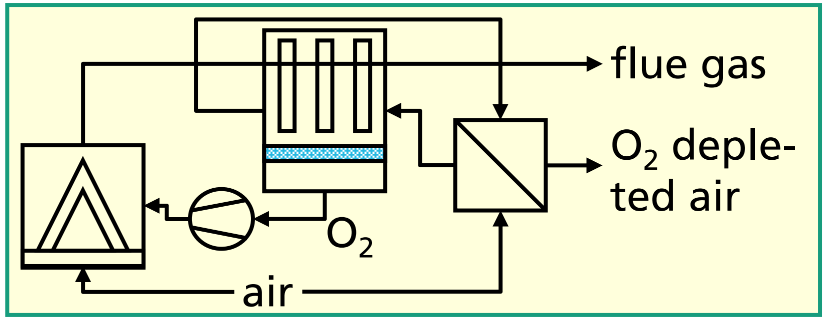
Atmospheric Combustion:
Air vs. Oxyfuel

O_2 enrichment: thermal loss↓, heat transfer↑, **fuel saving ≤ 50 %** (depends on $T_{waste\ gas}$, p_{O2} …)

- **thermal integration** for $T_{waste\ gas}$ **> 850 °C**

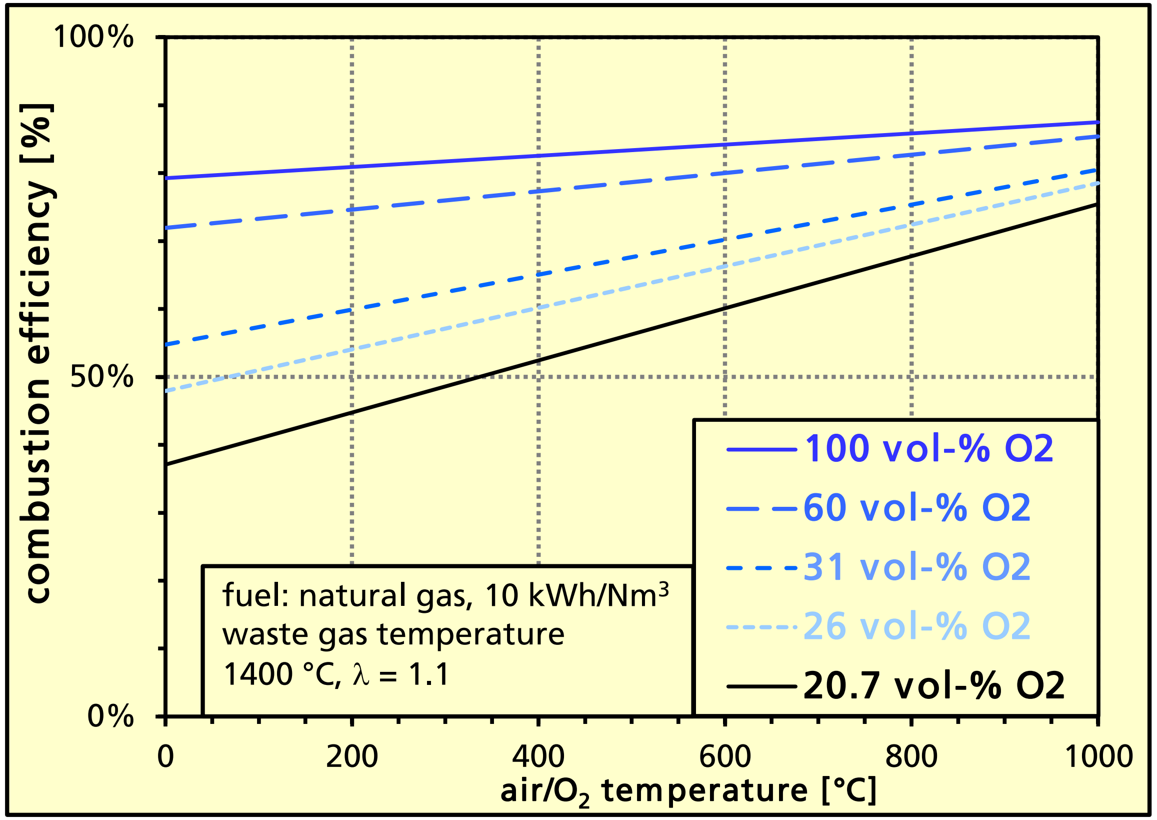


→ Ibis

→ DeSa

- **0.15 - 0.3 $kWh_{el.}/Nm^3$ O_2**

cryo: ≥ **0.46**
PSA: ≥ **0.9**



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Atmospheric Combustion:
Energy demand for Fuel Saving

CCS always increase energy demand?

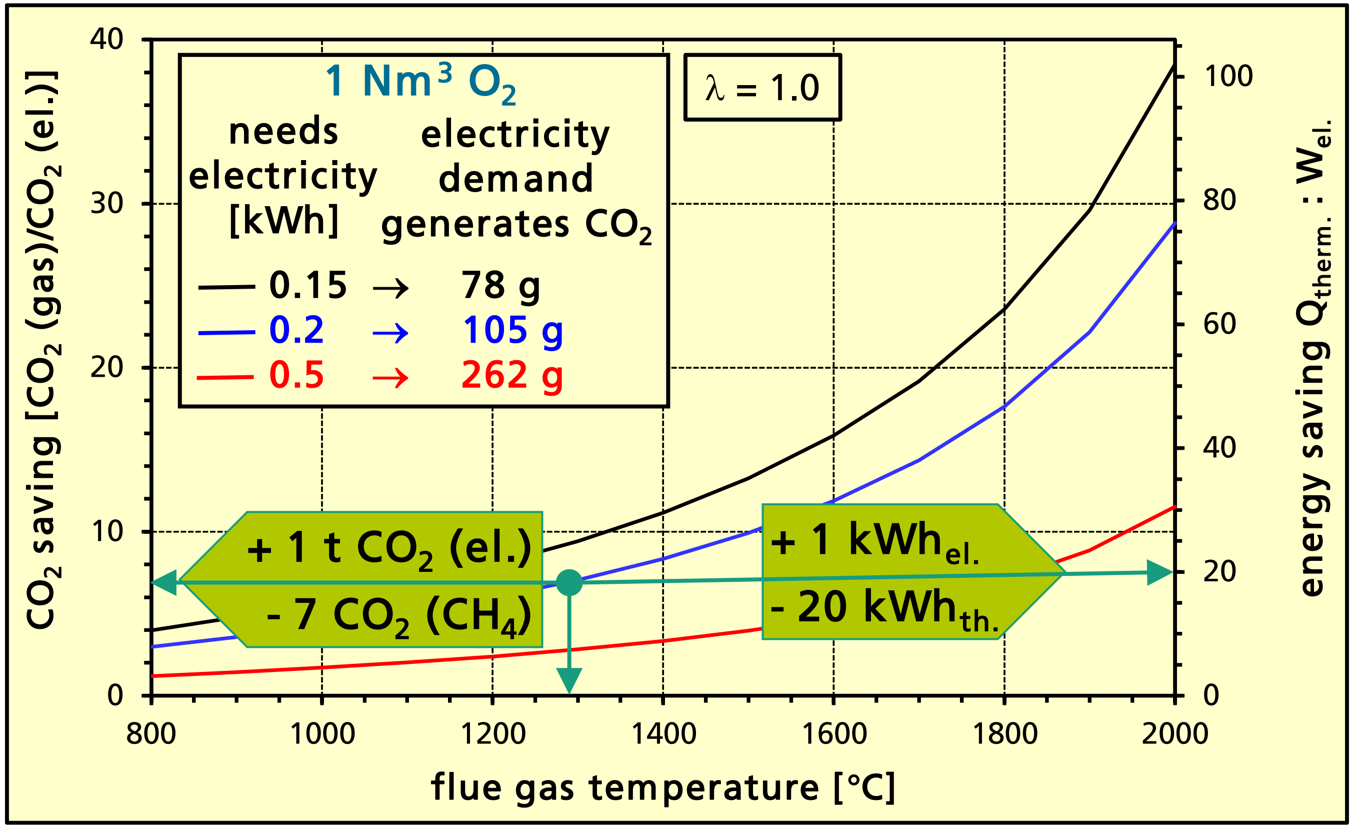
- O_2↑ enables lower gas throughput and heat losses
- same heat but less fuel
- fuel saving = f (T, λ, energy 1 m³ O_2)

kWh$_{el.}$/m³ O_2

- cryo ASU: ≈ 0.5 → Ibis
- MIEC typically: ≈ 0.2 → DeSa
- MIEC min.: ≈ 0.15

- CO_2 capture with energy saving!
- most promising CCS route

CO_2 emissions (Germany):
by electricity production: 523 g/kWh
by gas combustion: 197 g/kWh



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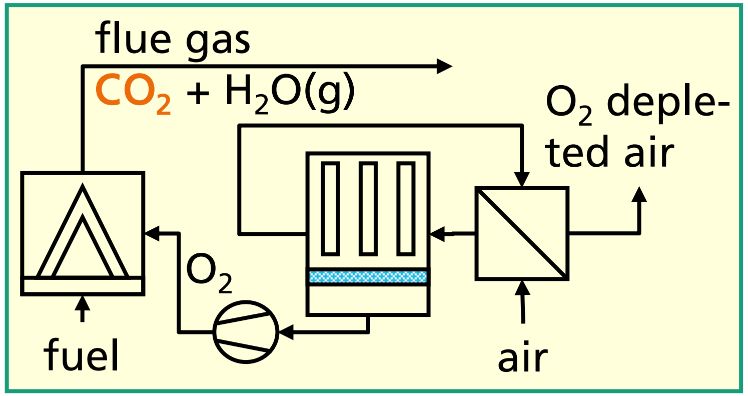
Atmospheric Combustion:
Separate MIEC Plant: CO_2 abatement Costs for Oxyfuel

Oxyfuel-CCS with local O_2 production:

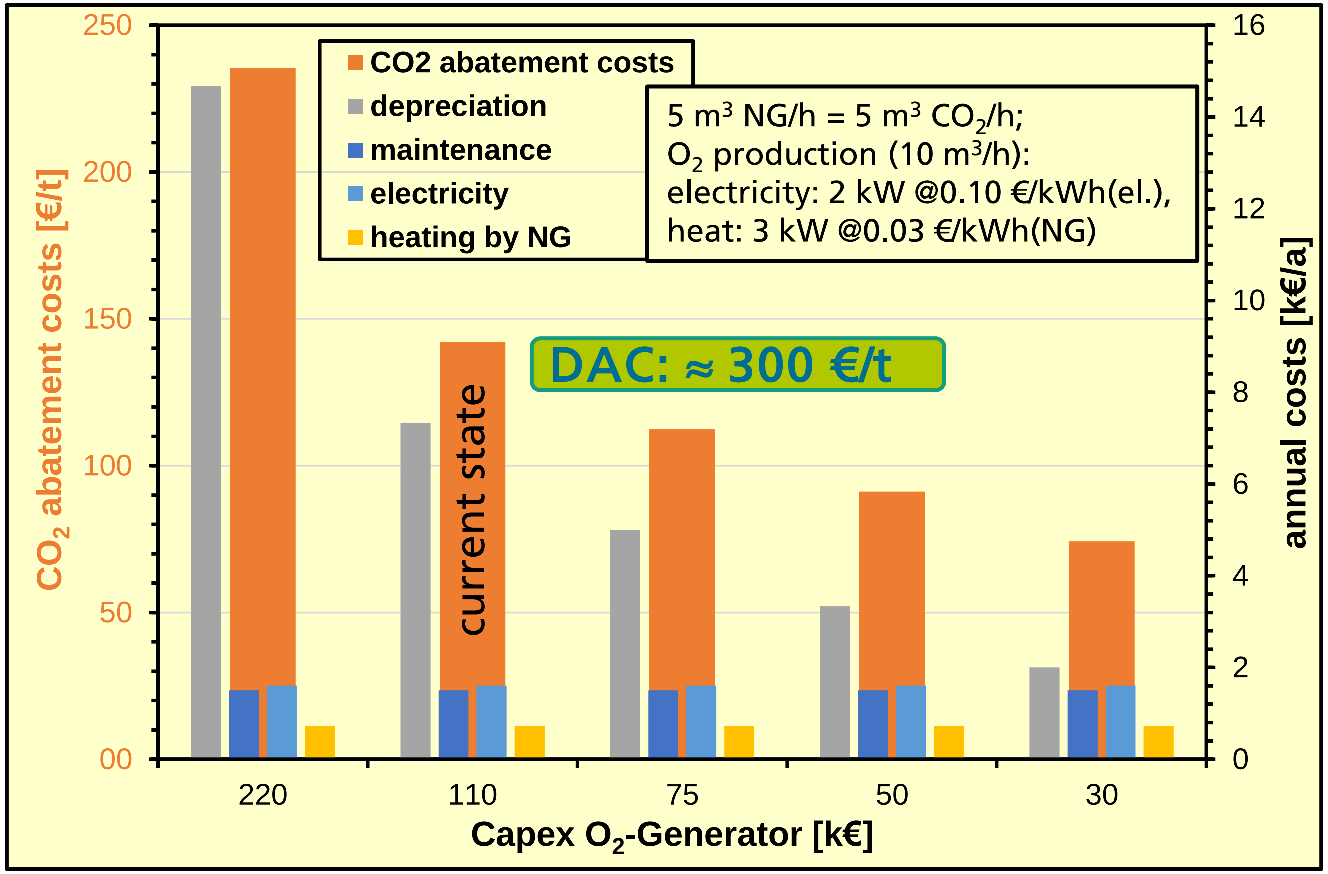
- **separately**, no thermal integration
- **depreciation** determines **CO_2 costs**



➤ further **decrease of CAPEX!**

- **limited capacity** for **large plants**

not yet established



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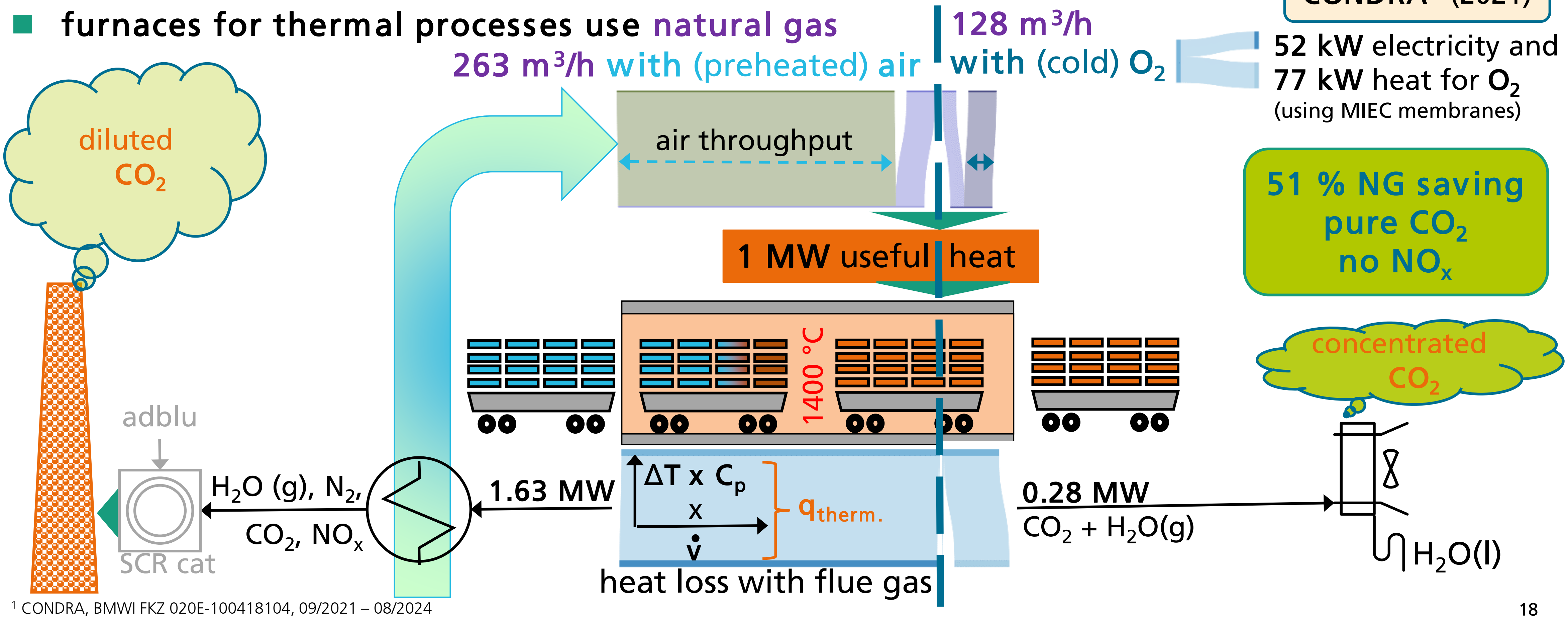
Atmospheric Combustion:
Integrated MIEC Plant: Energy Saving & CO_2 Capture

- furnaces for thermal processes use natural gas



[1] CONDRA, BMWI FKZ 020E-100418104, 09/2021 – 08/2024

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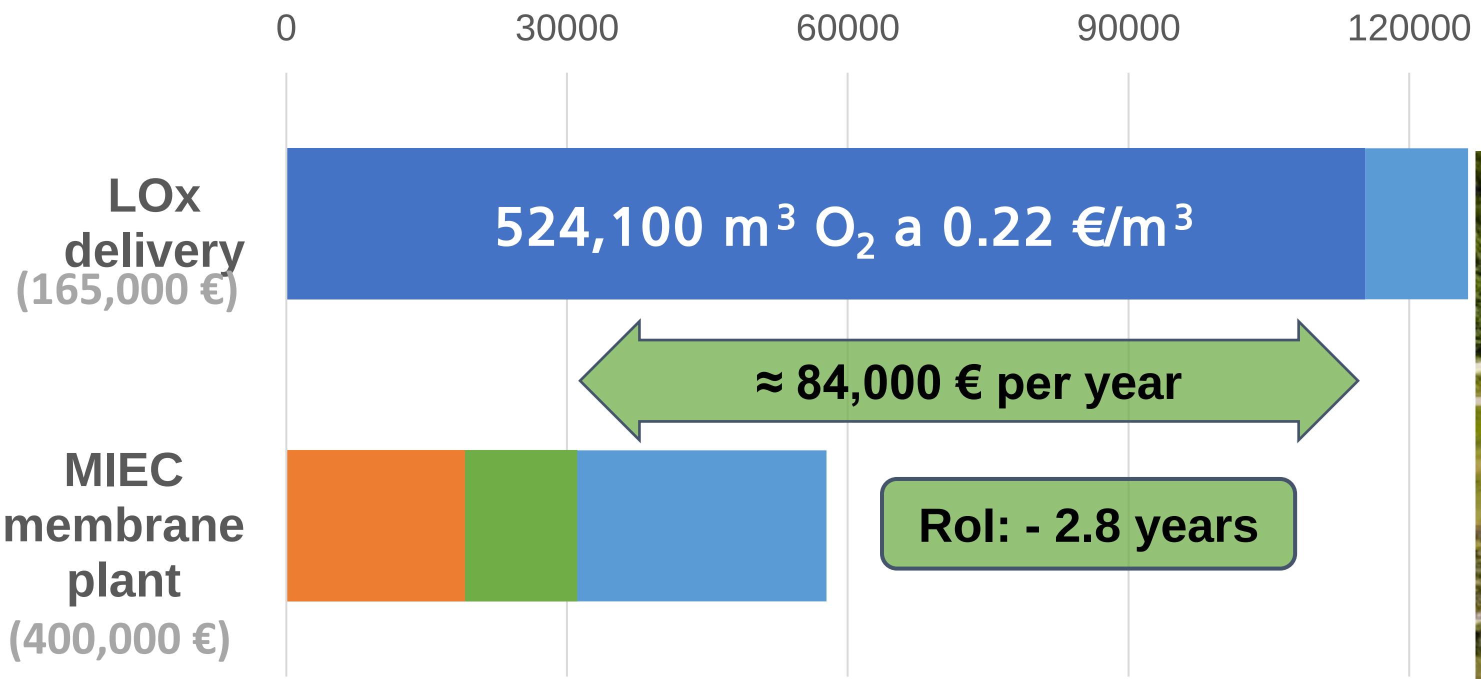
Market Entry:
Sewage Plants: Ozone Post Treatment – Economic Benefit

- Sewage Plant Aachen-Soers[1] - annual LOx costs:



CO_2–Emissionen: - 80%

[1]Brückner, I.: Großtechnische Umsetzung einer Ozonung zur Vollstrombehandlung auf der Kläranlage Aachen-Soers. 28.11.2017. 43. Berliner Wasserwerkstatt

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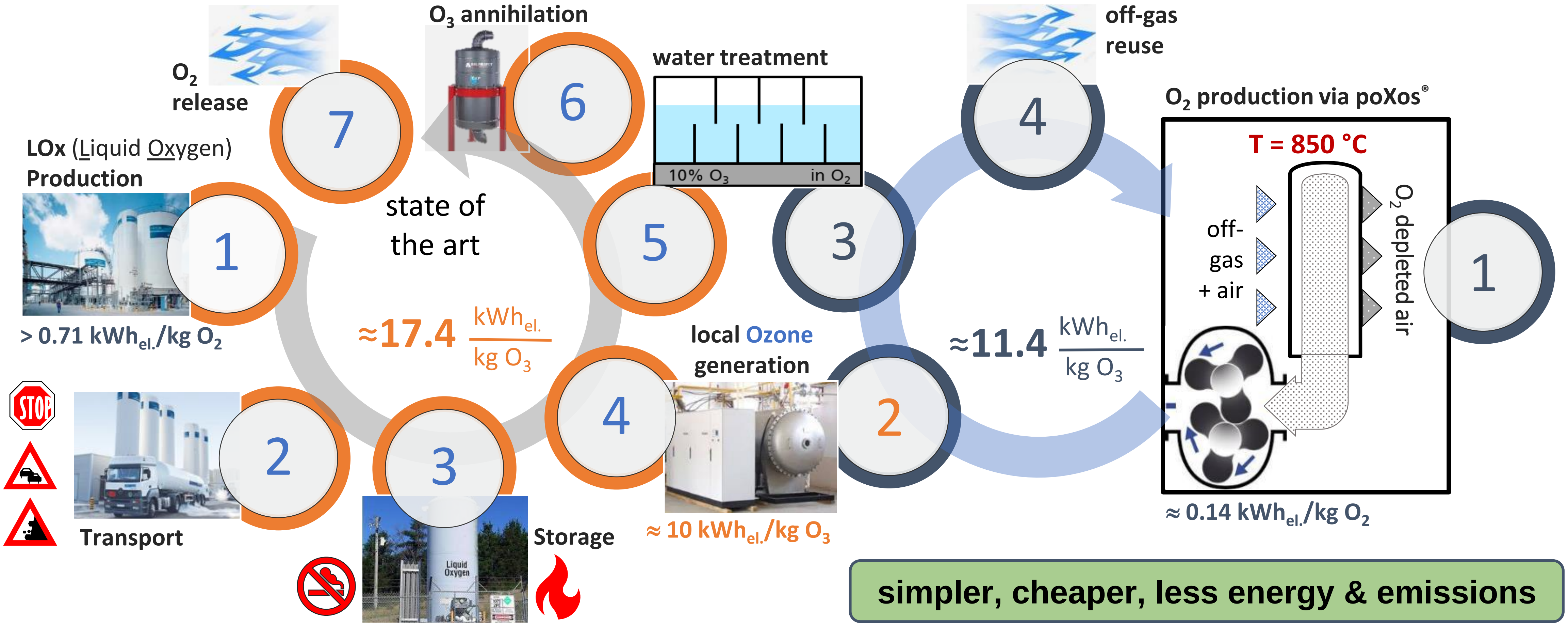
Market Entry:
Sewage Plant: Ozone Treatment – Process Comparison



simpler, cheaper, less energy & emissions

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Spin-Off Company POXOS®:
The Best of both Worlds

Cryogenic ASU (best of Linde):
0.46 kWh/m³ @>30,000 Nm³ O_2/h

pure Oxygen, but transport

high CAPEX, relatively low energy demand, pure O_2

POXOS®

best of both worlds!

cheap heat + less electricity

OPEX ↓ | on-site | O_2 purity ↑

less CO_2: 50 … 100 %

patented process | unique material and components

✓ **Freedom to Operate**

PSA generator:
0.9 kWh/m³ @< 0.1 Nm³ O_2/h

on-site, but high electricity costs

high OPEX, low purity < 95 % O_2

Customer benefit increases with decreasing O_2 costs.
Competitiveness benefits from lower energy demand, scalability and reduced CO_2 emissions.

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