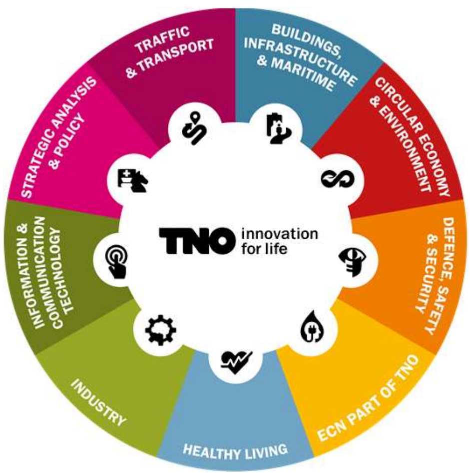
VALORISATION OF STEEL OFF-GASES TO ENABLE ECONOMIC VIABLE CO_2 STORAGE AND UTILIZATION

Jaap Vente,
TALLINN, 23 OCTOBER 2019

TNO MISSION AND ORGANISATION

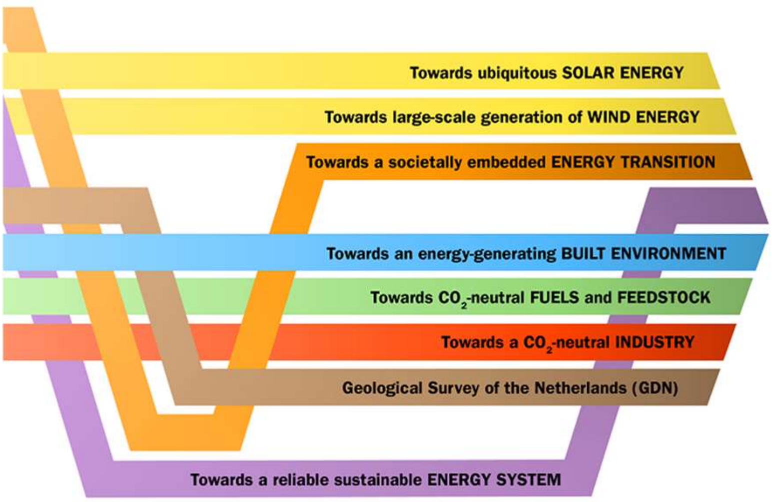
- TNO connects people and knowledge to create innovations that boost the competitive strength of industry and the wellbeing of society in a sustainable way.
- We have been using our knowledge and experience for more than eighty years.
- 'INNOVATION FOR LIFE'



ECN.TNO ENERGY INNOVATIONS IN THE NETHERLANDS

- Covering all parts of energy supply, use and management
- ~700 employees
- 100 M€/y turn over

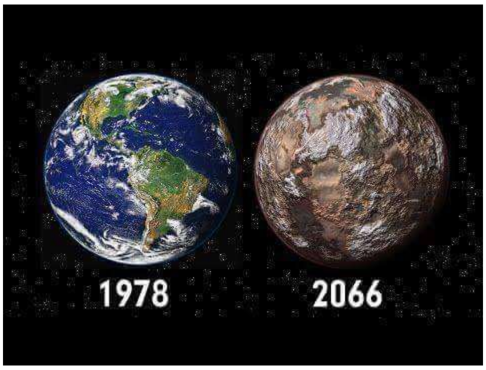
PROGRAMMATIC APPROACH



INDUSTRIAL TRANSFORMATION

Vision towards sustainable, economic robust and CO_2 neutral industry.

DRIVER FOR INDUSTRIAL TRANSFORMATION



The General Consensus

@Chimborazo, Ecuador
5000m above sea level

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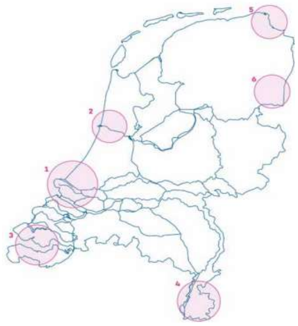
REQUIRED MEASURES

MANY OPTIONS MANY MEASURES

- Energy efficiency improvement existing processes
- New (inherently more efficient) processes
- Renewable feedstock (biobased industry)
- Electrification, hydrogen and CO_2 use
- Carbon Capture & Storage (with BECCS negative GHG emissions)
- Recycling/re-use/circular value chains
- Shifts in markets and products
- Industrial symbiosis



Location and size of the main industrial emission clusters.
1) Rotterdam - Moerdijk (16.9 Mt CO_2)
2) Noordzeekanaalgebied (12.0 Mt CO_2)
3) Zeeland - W-Brabant (7.9 Mt CO_2)
4) Chemelot (4.5 Mt CO_2)
5) Eemsdelta (0.7 Mt CO_2)
6) Emmen (0.5 Mt CO_2

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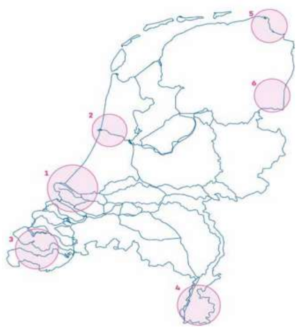

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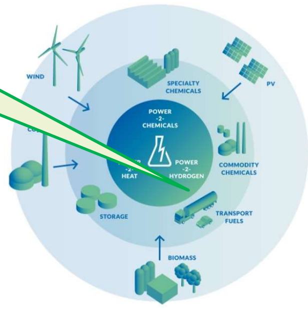
ELECTRIFICATION AND CO_2 USE

Generic points of attention

- Energy efficiency
  electrification is not an energy saving option by definition
- Speed of implementation
  long term option
- 2D nature of electrochemistry
  costly scale up
- Availability of electricity
  connectivity grid sizes etc.
- Availability of renewable electricity
  hydro, wind, solar, biomass....

Power to advanced fuels

CO_2 reduction with green H_2	Direct CO_2 reduction
✓ Electrolysis of H_2O ✓ Synthesis of alcohols and dimethylether	✓ Production of formic acid ✓ Combined reduction of CO_2 and H_2O



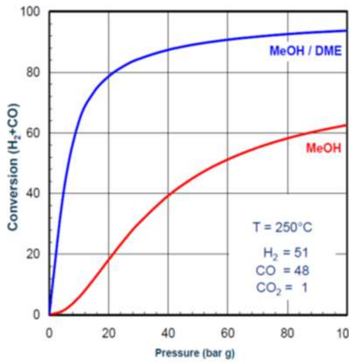
DME: THE ADVANCED FUEL FROM RENEWABLE RESOURCES

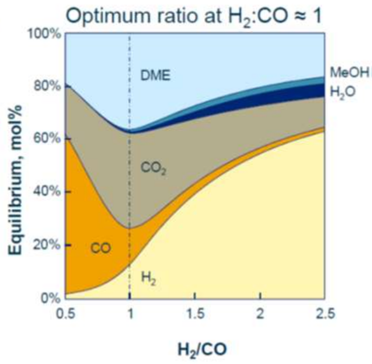
THERMODYNAMIC LIMITATIONS

- Conversion from CO and H_2 is limited
- Excess oxygen can be bound to carbon and to hydrogen

$$3H_2 + 3CO \leftrightarrow C_2H_6O + CO_2$$
$$4H_2 + 2CO \leftrightarrow C_2H_6O + H_2O$$

- Conversion from CO_2 and H_2 is minimal
- Excess oxygen must be bound to hydrogen





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CO_2 SENSITIVITY

- Thermodynamics favor removal of excess through CO_2 formation
- Carbon efficiency is expected to become leading

- CO_2 conversion requires the formation of H_2O as the byproduct
- How to push the DME formation reaction to form H_2O?

- Catalyst won't help

Bill Clinton famously captured the essence of process intensification in 1992

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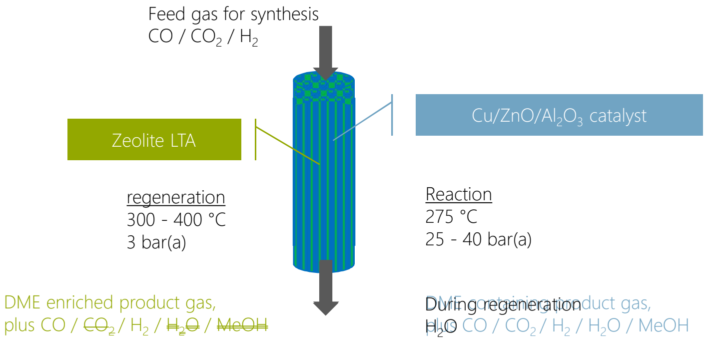
SORPTION ENHANCED DIRECT DME SYNTHESIS



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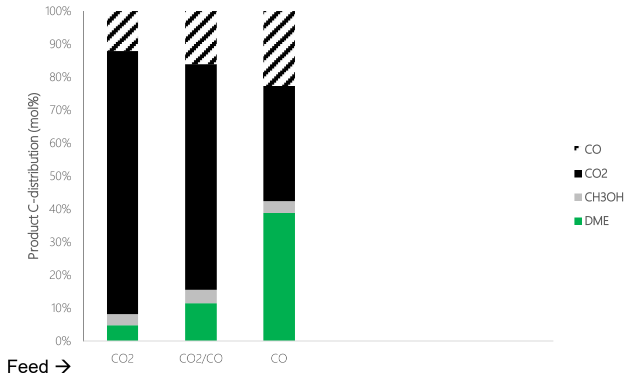
FEED FLEXIBILITY

- Direct DME synthesis
- 275 °C & 40 bar(a)
- Thermodynamic equilibrium
- Carbon is found in CO / CO_2 / MeOH / DME



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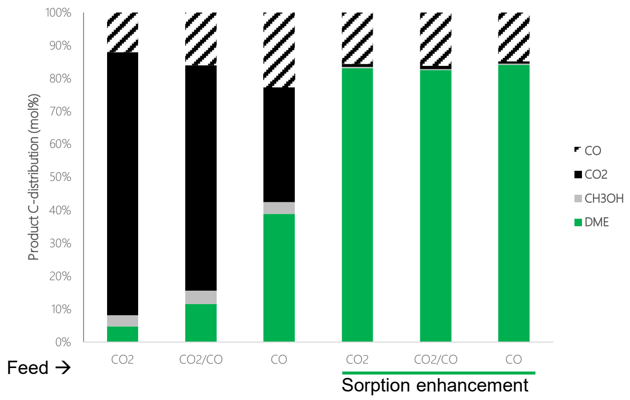
FEED FLEXIBILITY

- Direct DME synthesis
- 275 °C & 40 bar(a)
- Thermodynamic equilibrium
- Carbon is found in CO / CO_2 / MeOH / DME

- Sorption-enhanced DME synthesis
- 275 °C & 40 bar(a)
- Experimental results
- Carbon is found in CO / ~~CO_2 / MeOH /~~ DME



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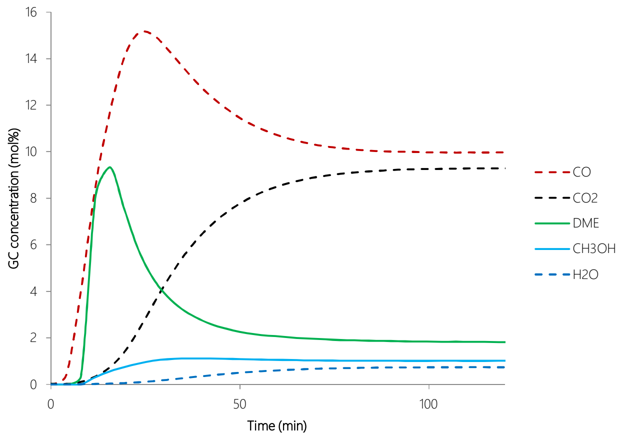
REGENERATION CONDITIONS

- Catalyst & sorbent regeneration at **300 °C**

- CO_2:CO = 1:2
- $M = \frac{([H_2]-[CO_2])}{([CO]+[CO_2])} = 2$
- 275 °C & 25 bar(a)



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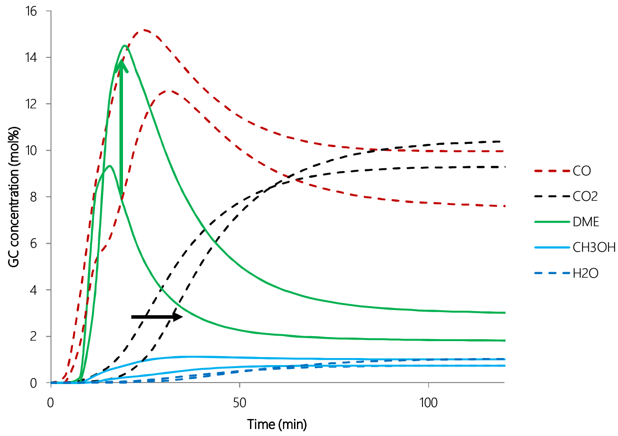
REGENERATION CONDITIONS

- Catalyst & sorbent regeneration at 400 °C
- CO_2:CO = 1:2
- $M = \frac{([H_2]-[CO_2])}{([CO]+[CO_2])} = 2$
- 275 °C & 25 bar(a)
- The more severe regeneration procedure results in increased performance



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ENERGY CONTAINING RESIDUAL STREAMS

- Unique feature of current steel making processes
- Presence of diluted energy containing streams

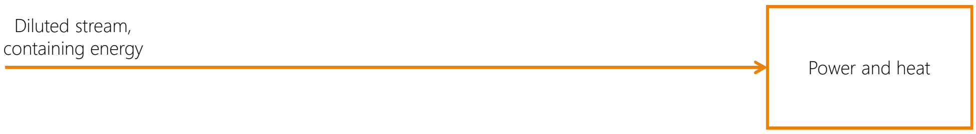
Gas type	CO_2	CO	N_2	H_2	CH_4	LHV (MJ/Nm^3)
BFG	22	22	49	4	--	3.2
BOFG	14	57	14	3	--	7.5
COG	2	5	7	62	24	15.3

HOW TO VALORIZE THE ENERGY IN THE RESIDUAL STREAM?

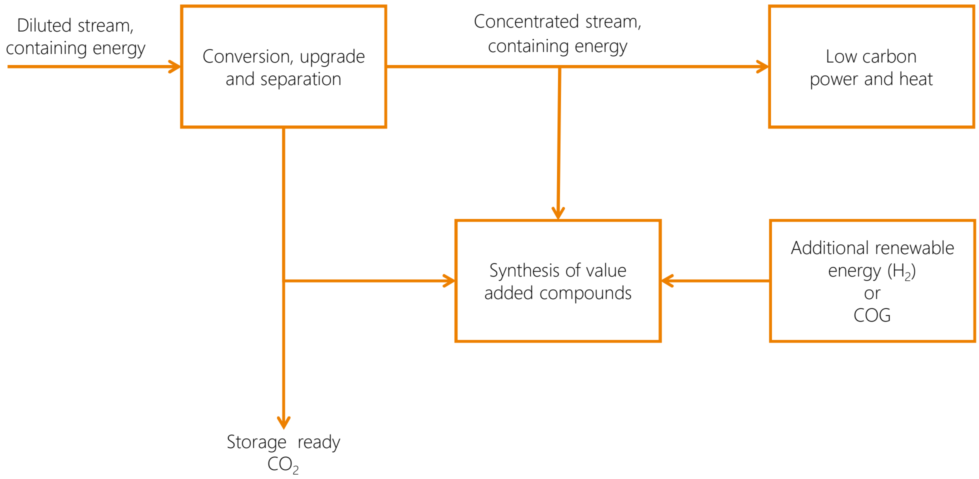
- BFG – Blast Furnace Gas
- BOFG – Basic Oxygen Furnace gas
- COG – Cokes Oven gas

see IEAGHG report on Iron&Steel,
http://www.ieaghg.org/docs/General_Docs/Reports/2013-04.pdf

BASE CASE



CCUS APPROACH



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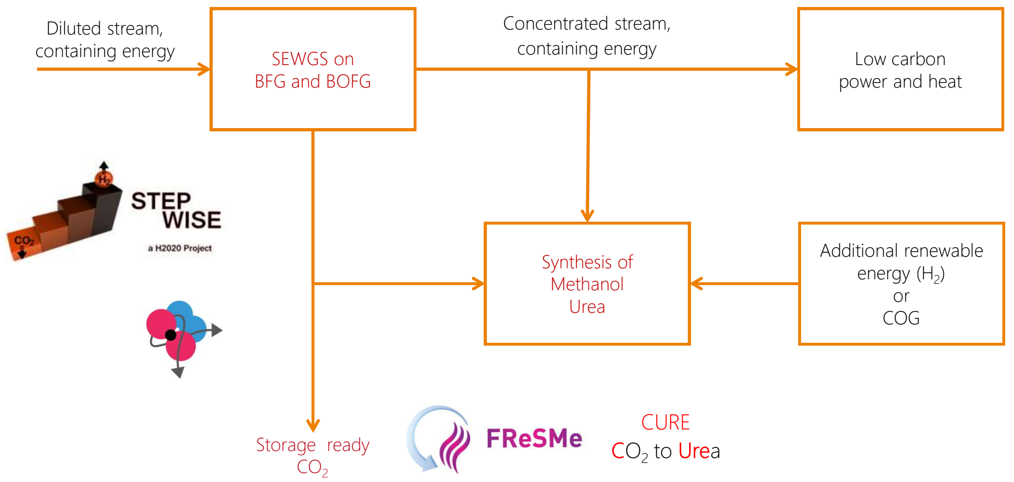
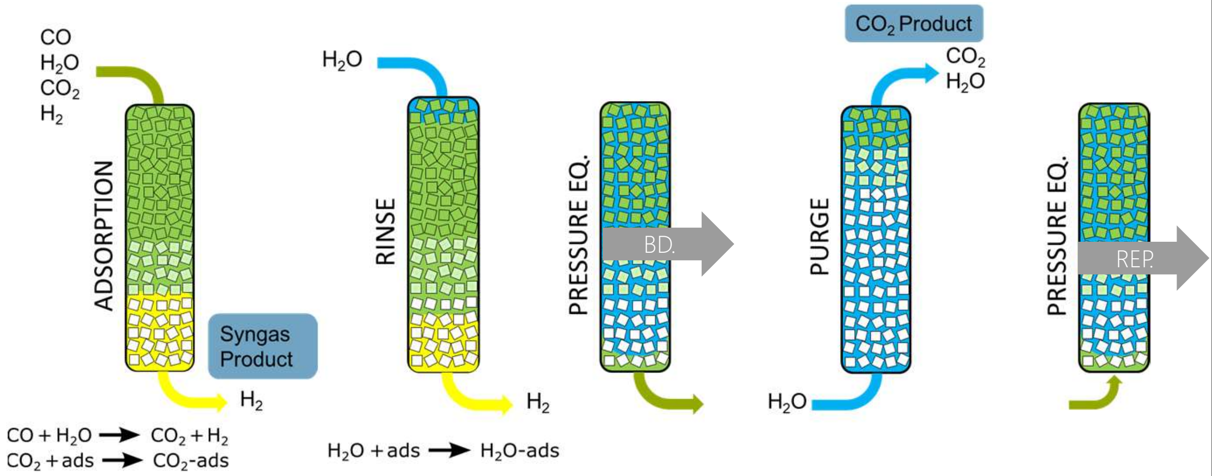


REACTIVE PSA OPERATION



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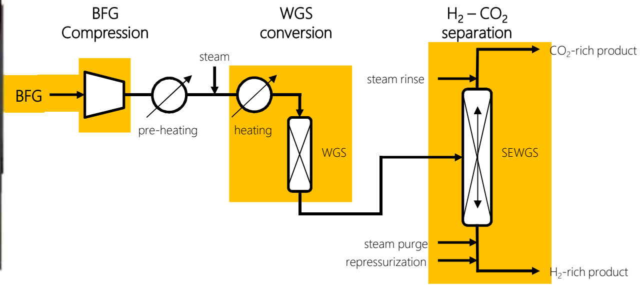
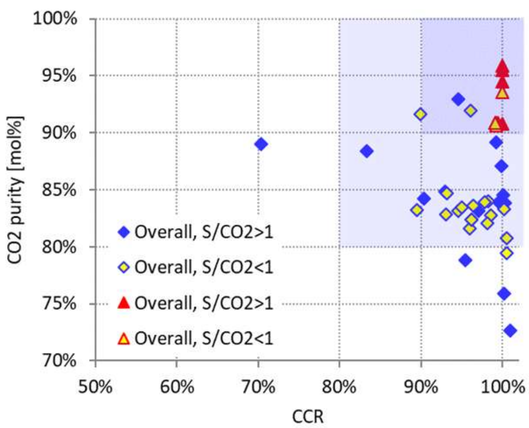
CAPTURING CO_2 IN THE STEEL INDUSTRY

STEPWISE PILOT LAY-OUT



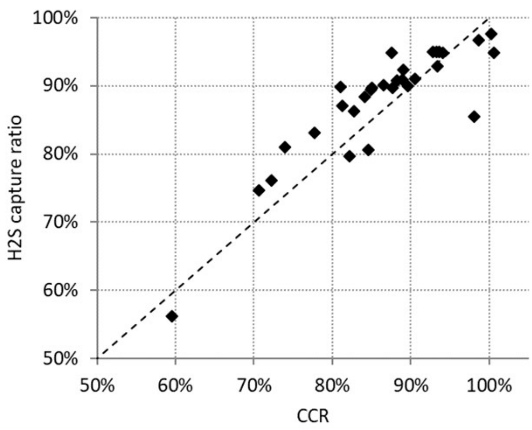
CAPTURING PERFORMANCE

- Cyclic performance mapping
  - Carbon Capture Ratio
  - CO_2 purity
  - Rinse & Purge steam usage per CO_2 avoided
- 1st campaign results
  - Mapping
- 2nd campaign initial results
  - Optimization



EFFECTIVE SULPHUR REMOVAL

- Reversible sorption of H_2S
  - No influence on CCR, purity, steam
  - High CCR = high SCR
  - Simultaneous sulphur and carbon removal
  - H_2S ends up in CO_2 product
  - H_2S slip prior to breakthrough < 1 ppm,wet



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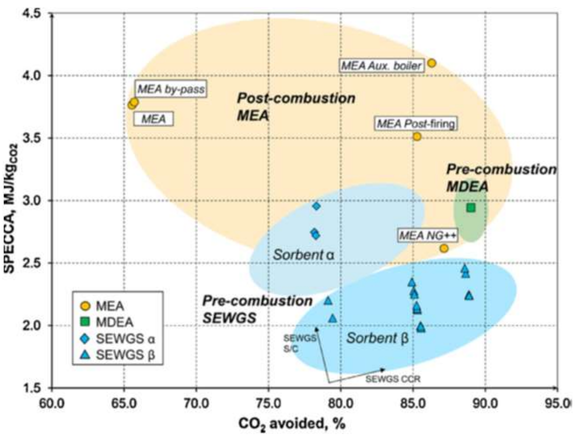
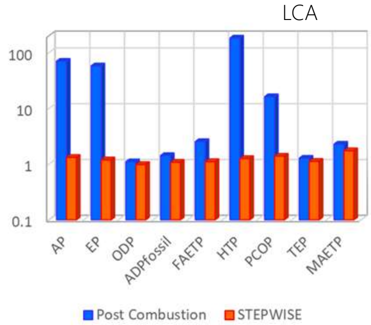
ADVANTAGES STEPWISE TECHNOLOGY

Iron and Steel



International Journal of Greenhouse Gas Control, 2015, 41, 249

LCA



Journal of Cleaner Production, 2019, 211, 1015

Refinery

	Base Case	Base case + amine	SEWGS
H_2 purity	>99.5%		
CO_2 purity	n/a	>99%	>99%
Feed + Fuel (kmol/h)	100	93.2	91.6
Energy Efficiency (ΣLHVout/ΣLHVin)	79.4%	77.8%	81.2%
CO_2 emitted	100	39	35

10thEuropean Congress of Chemical Engineering 2015

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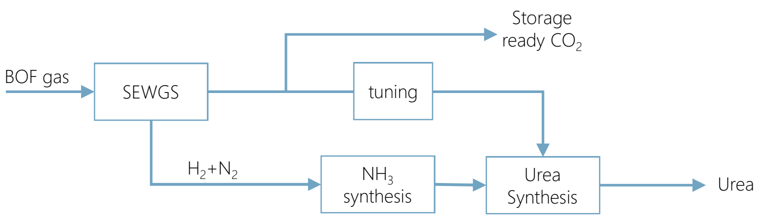
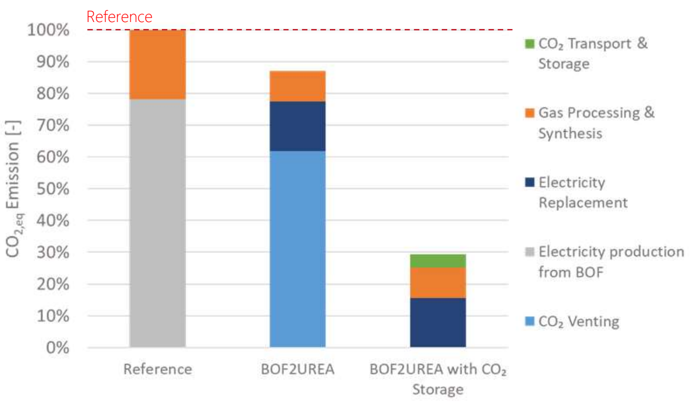
UREA PRODUCTION FROM BOFG

- ~55% of globally produced H_2 is used for NH_3
- Residual gases in the steel industry contain N_2
- After STEPWISE technology
  - N_2 goes with the H_2
  - Treated BOF gas has the right H_2/N_2 ratio for ammonia synthesis



LIFE CYCLE ANALYSIS

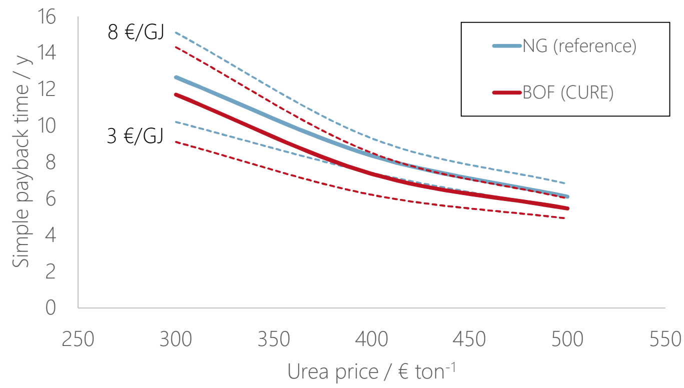


- Global Warming Potential (GWP) reduction of ~13% without CO_2 Storage.
- 70% $CO_{2,eq}$ avoided if deployed with storage and transport.
- Electricity consumption is the primary source of remaining $CO_{2,eq}$.

ECN › TNO innovation for life

BUSINESS CASE

- Comparable economics for natural gas based and BOF-gas based urea
- Urea pays for capture technology, storage ready CO_2 as side product



ACKNOWLEDGEMENTS

STEP WISE a H2020 Project

FLEDGED

The projects have received funding from the European Union's Horizon 2020 research and innovation program under grant agreements

No. 640769 — No. 727600

www.stepwise.eu — www.fledged.eu

2015 – 2019 — 2017 – 2020

The ELEGANCY project has received funding from the ERANET program Accelerating CCS Technologies

https://www.sintef.no/elegancy

2017 – 2020

The CURE project has received funding from RvO under grant agreement TES 1216120

CURE
CO_2 to Urea

2016

Accelerating CCS Technologies

Rijksdienst voor Ondernemend Nederland

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