Pre combustion CO_2 capture

Daniel Jansen

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Energy research Centre of the Netherlands

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2nd international workshop: CCS and CCU in Germany, The Netherlands, Norway, Poland and Scotland - Challenges and Changes

Düsseldorf, Germany, 2011, 9th/10th November

Pre-Combustion CO_2 Capture

- Removes carbon from the fuel before combustion
  - -Carbon is captured in the form of CO_2
  - -**Hydrogen is the resulting fuel**

- Well known process used for H_2 generation for > 50 years

- Currently used to produce high-purity H_2 for chemical and refining uses

This presentation focus on coal

Pre-Combustion CO_2 Capture

Today

- Technologies for hydrocarbon conversion
- Variety of gas treating technologies available

  → **High energy penalty**

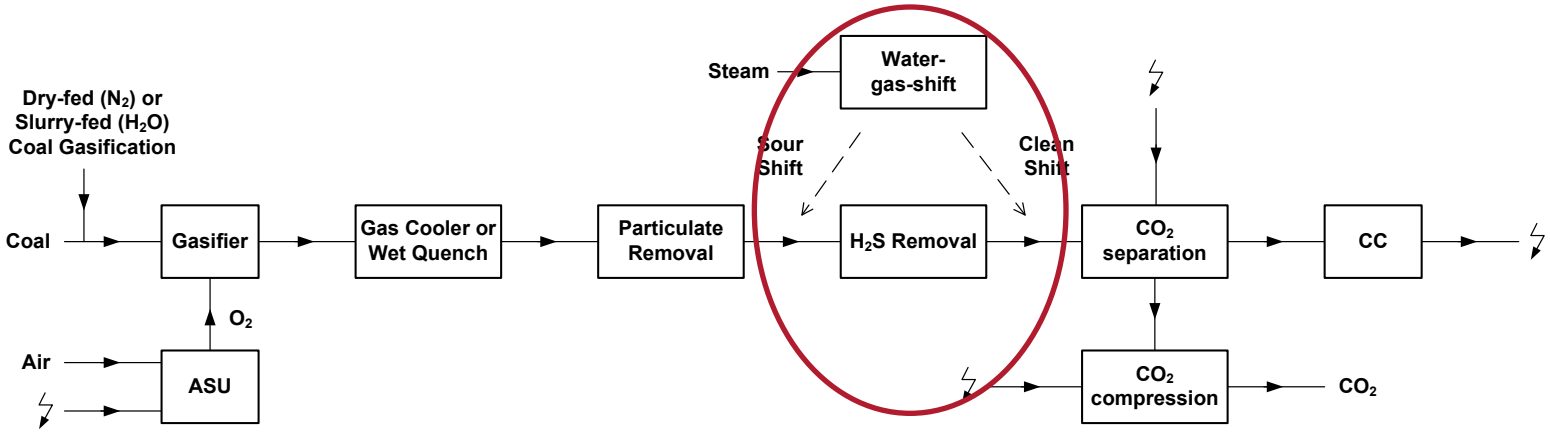
Developments to reduce energy penalty

- Advanced solvents
- Advanced shift
- Reaction/separation integration: SEWGS

Pre combustion capture as of today

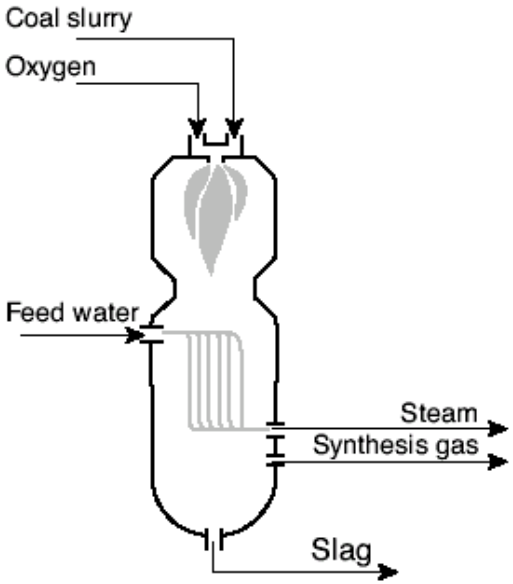
- In Combined cycles; **large scale deployment NGCC**
  - Reforming and gas separation technologies commercial available

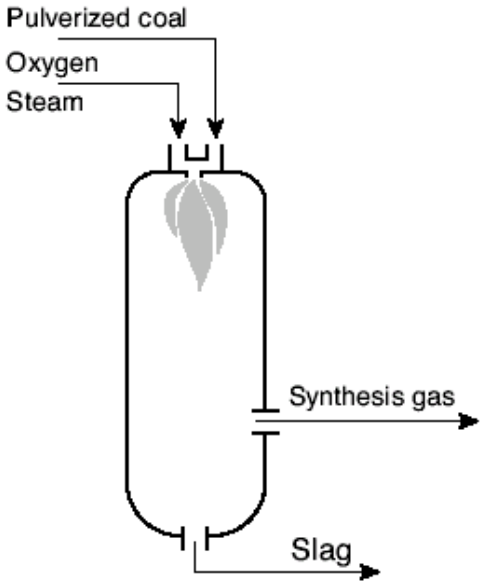
- In IGCC; **no large scale deployment of IGCC**
  - Gas separation technologies commercial available
  - More experience in ammonia, chemicals production, esp. in China

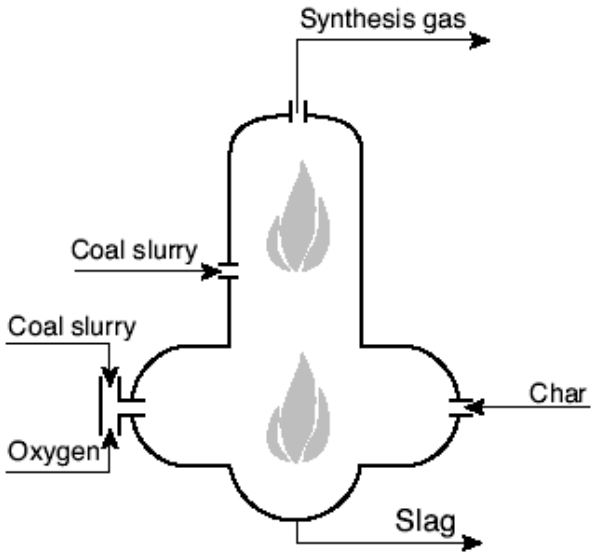


Pre-Combustion Coal fuelled systems

- Solid hydrocarbon conversion
  - Convert hydrocarbon into H_2, CO and CO_2.
  - This is done by gasification (GE, Shell, E-gas)

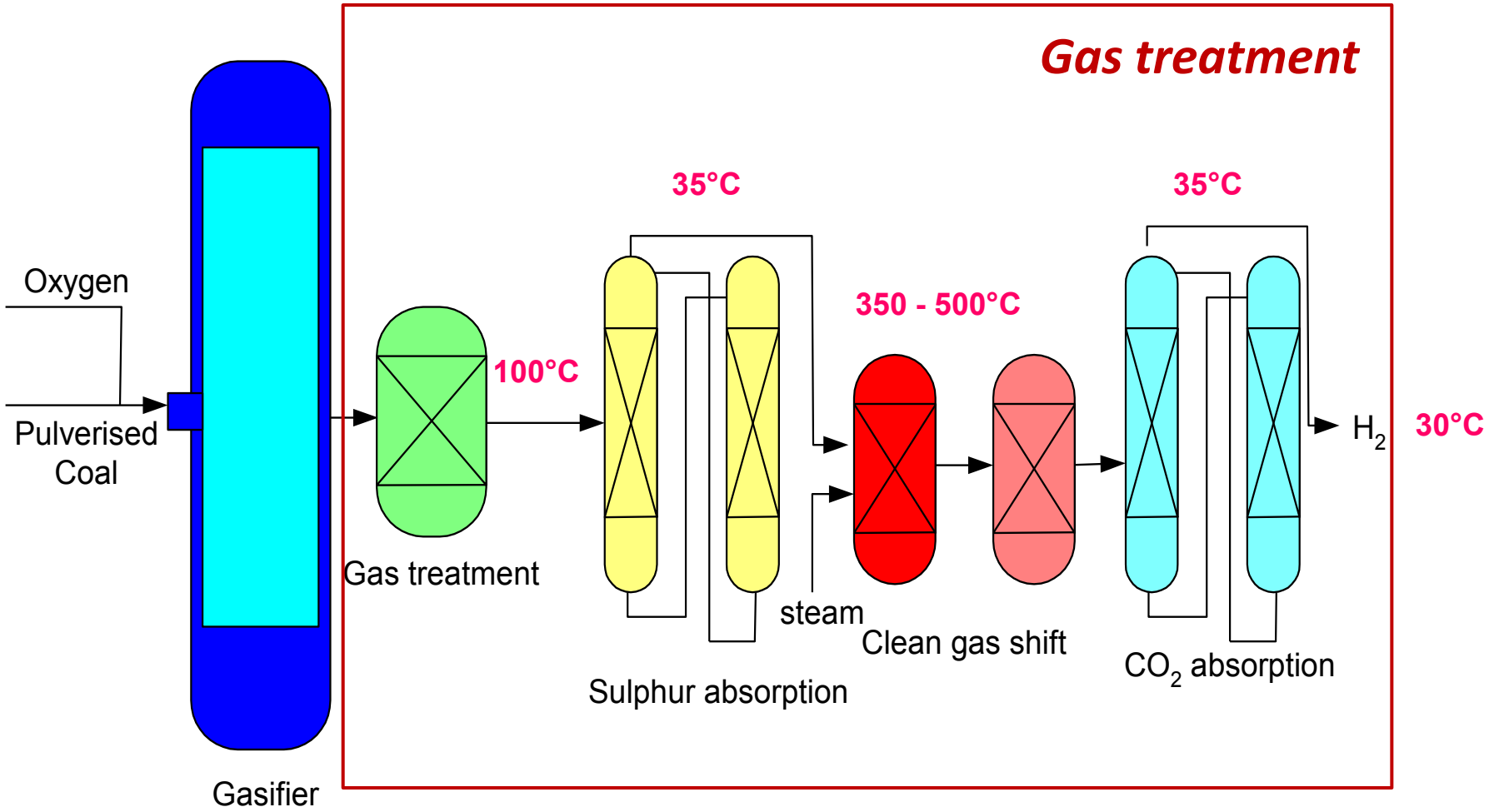






Source Oil & gas science and Technology, Vol 60, 2005 No.3

Pre combustion Gasification with carbon removal



Existing (sour) gas treating processes

		BASF	DOW	EXXON	Fluor	Linde	Lurgi	Shell	Uhde/IFP	UOP
Monoethanolamine	MEA		O	O			O			
Diethanolamine	DEA						O			
Diisopropanolamine	ADIP							O		
Methyldiethanolamine	MDEA	O	O					O		
Potassium carbonate	Hotpot		O	O			O			
Methanol+MDEA/DEA	Amisol						O			
XXX+MDEA	Flexsorb			O						
Sulfolane+MDEA/DIPA	Sulfinol							O		
DME of PE glycol	Selexol									O
Methanol	Rectisol					O	O			
N-Methylpyrrolidone	Purisol						O			
PE glycol + dialkyl ether	Sepasolv	O								
Propylene carbonate	Fluor solvent				O					
Tetrahydrothiophenedioxide	Sulfolane							O		
Tributyl phosphate	Estasolvan								O	

Chemical Mixed Physical

		BASF	DOW	EXXON	Fluor	Linde	Lurgi	Shell	Uhde/IFP	UOP
Monoethanolamine	MEA		O	O			O			
Diethanolamine	DEA						O			
Diisopropanolamine	ADIP							O		
Methyldiethanolamine	MDEA	O	O					O		
Potassium carbonate	Hotpot		O	O			O			
Methanol+MDEA/DEA	Amisol						O			
XXX+MDEA	Flexsorb			O						
Sulfolane+MDEA/DIPA	Sulfinol							O		
DME of PE glycol	Selexol									O
Methanol	Rectisol					O	O			
N-Methylpyrrolidone	Purisol						O			
PE glycol + dialkyl ether	Sepasolv	O								
Propylene carbonate	Fluor solvent				O					
Tetrahydrothiophenedioxide	Sulfolane							O		
Tributyl phosphate	Estasolvan								O	

Chemical Mixed Physical

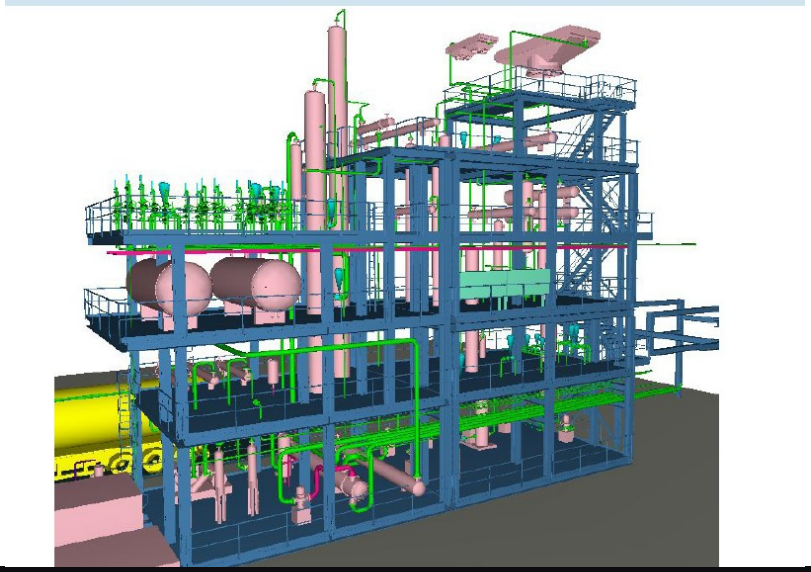
Gas solubility data at 1 atm, 25 °C (-30 °C methanol), vol gas/vol liq

Gas	Selexol	Fluor solvent	Purisol	Methanol
H_2	0.047	0.027	0.02	-
CO	0.10	0.072	0.075	-
C_1	0.24	0.13	0.26	-
C_2	1.52	0.58	1.36	-
CO_2	3.63	3.41	3.57	15
C_3	3.7	1.74	3.82	-
COS	8.46	6.41	9.73	-
NH_3	17.7	-	-	-
H_2S	32.4	11.2	36.4	92
nC_6	39.9	46.0	-	-
H_2O	2661	13640	14280	-
HCN	4356	-	-	-

Bucklin and Schendel (1985)
Hochgesand (1970)

1st generation pre-combustion capture: CO_2 CATCHUP project of Nuon

- CO_2 removal from side stream of existing IGCC plant in Buggenum, The Netherlands
- Water-gas-shift section + physical CO_2 sorbent
- ECN involved in conceptual design and catalyst testing

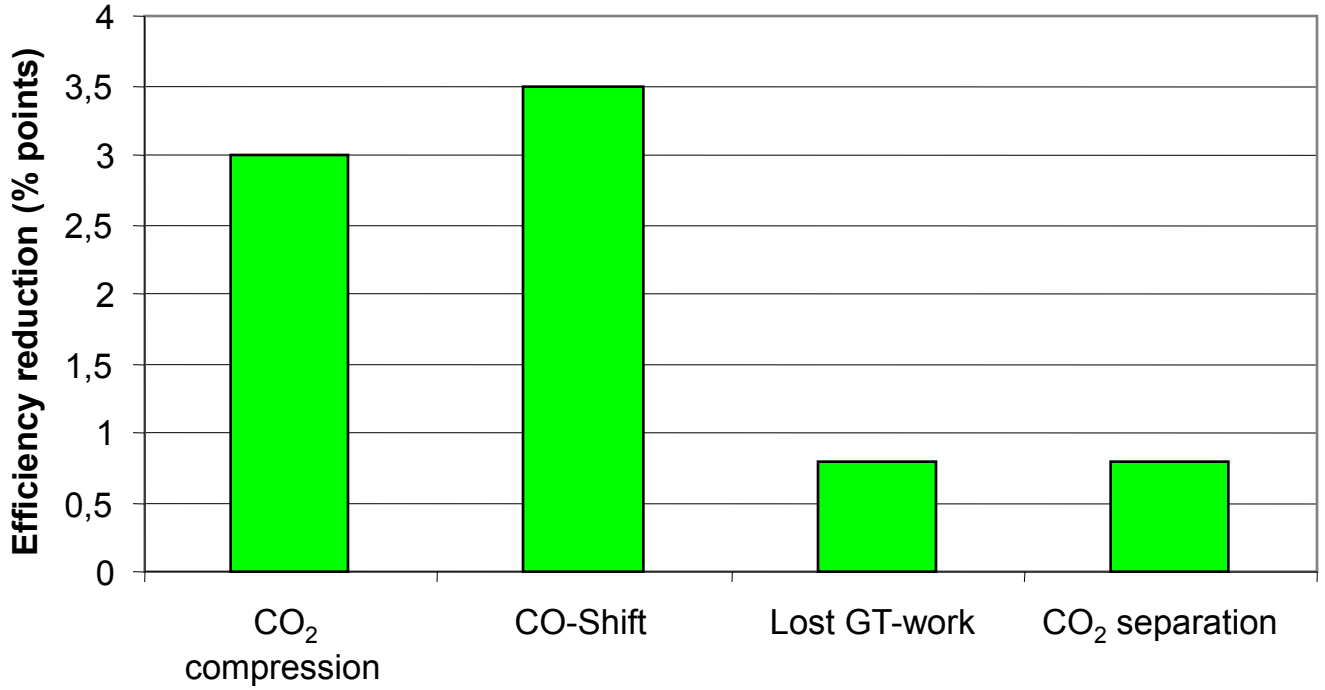


Catch-Up Pilot Plant, Buggenum

New Developments

pre-combustion: efficiency penalty capture

Losses due to CO_2 capture in IGCC with physical solvent

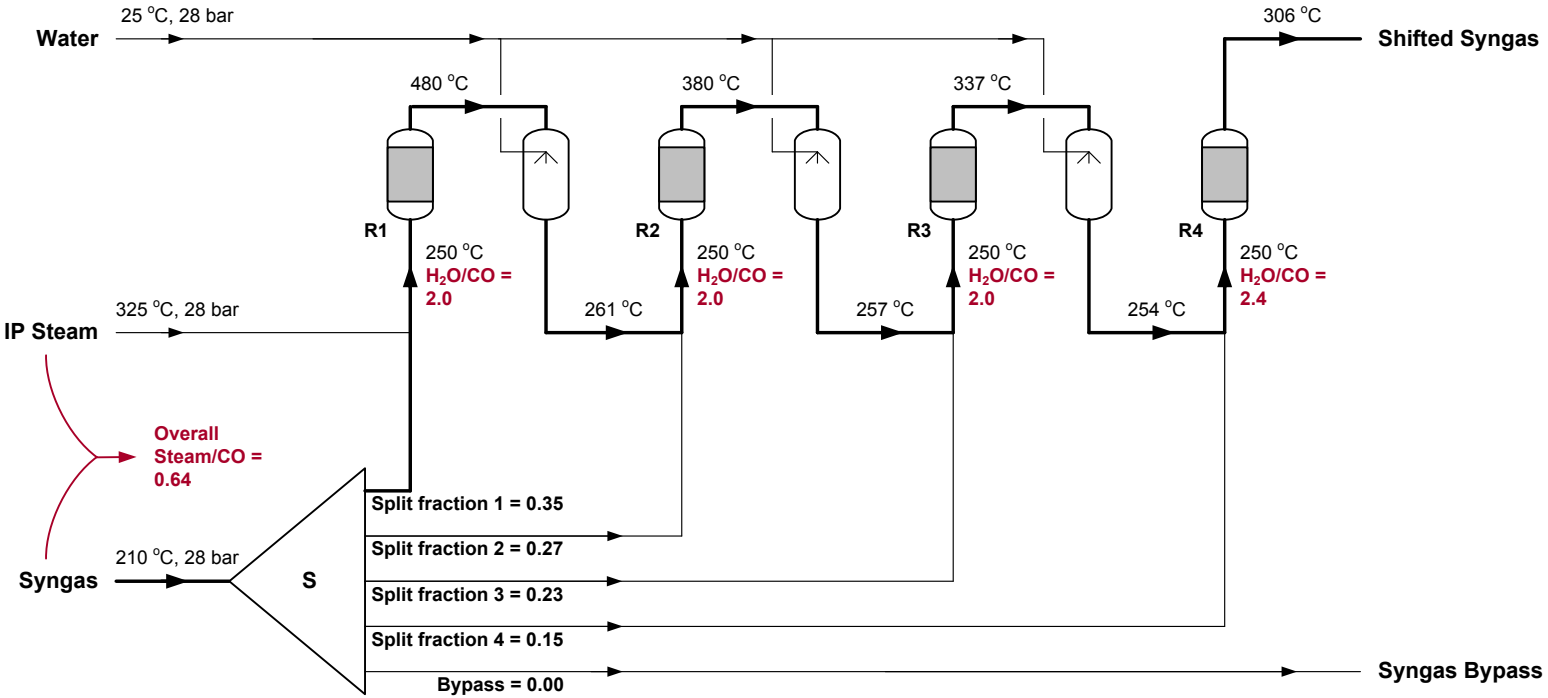


Improvements in CO_2 solvent process

Shell/Procede	New combinations of amines
TNO	Membrane-assisted desorption
TU Delft	Ionic liquids

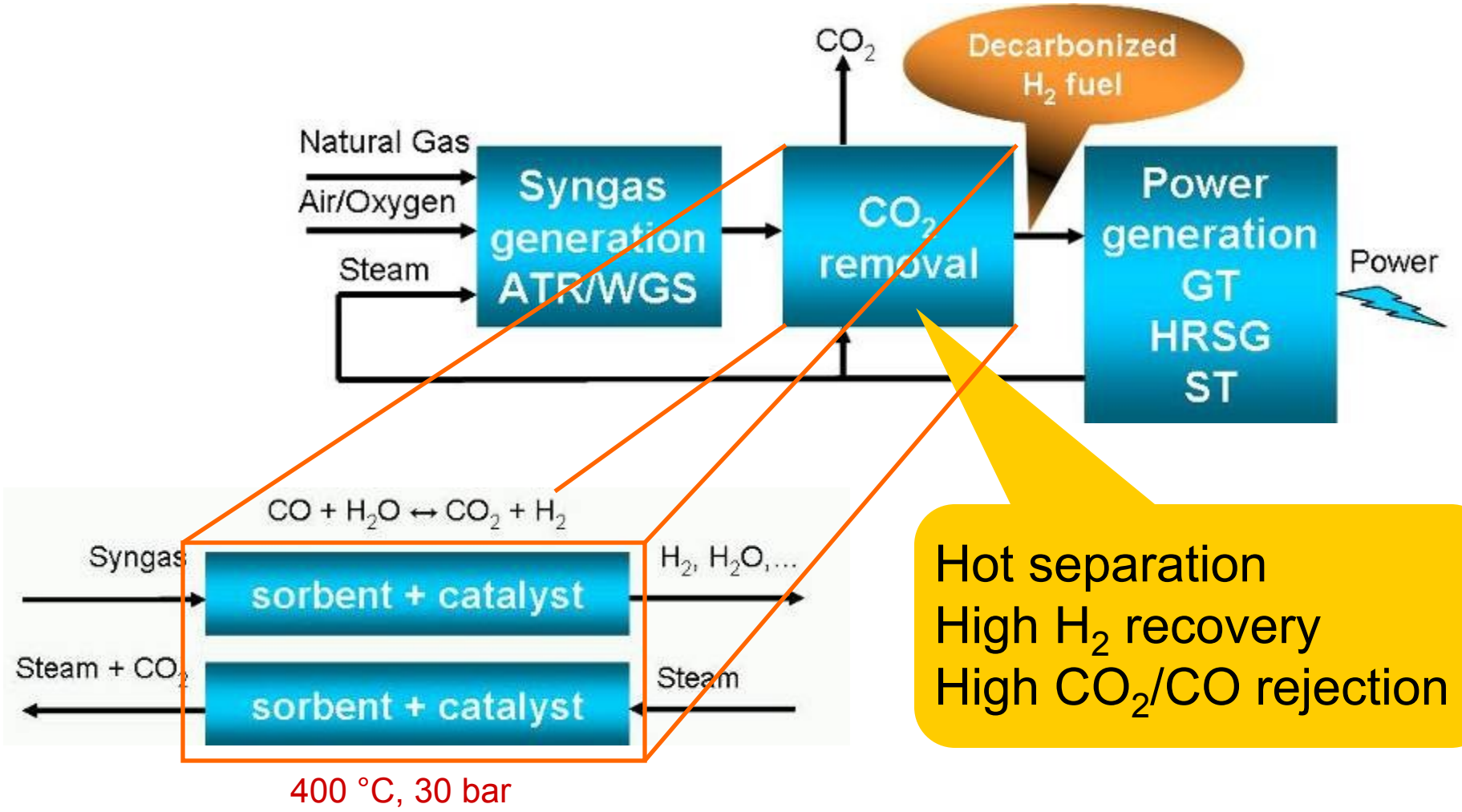
Advanced Shift: New scheme developed by ECN

- Advanced shift to reduce steam consumption
  - Overall steam/CO ratio reduced to 0,64



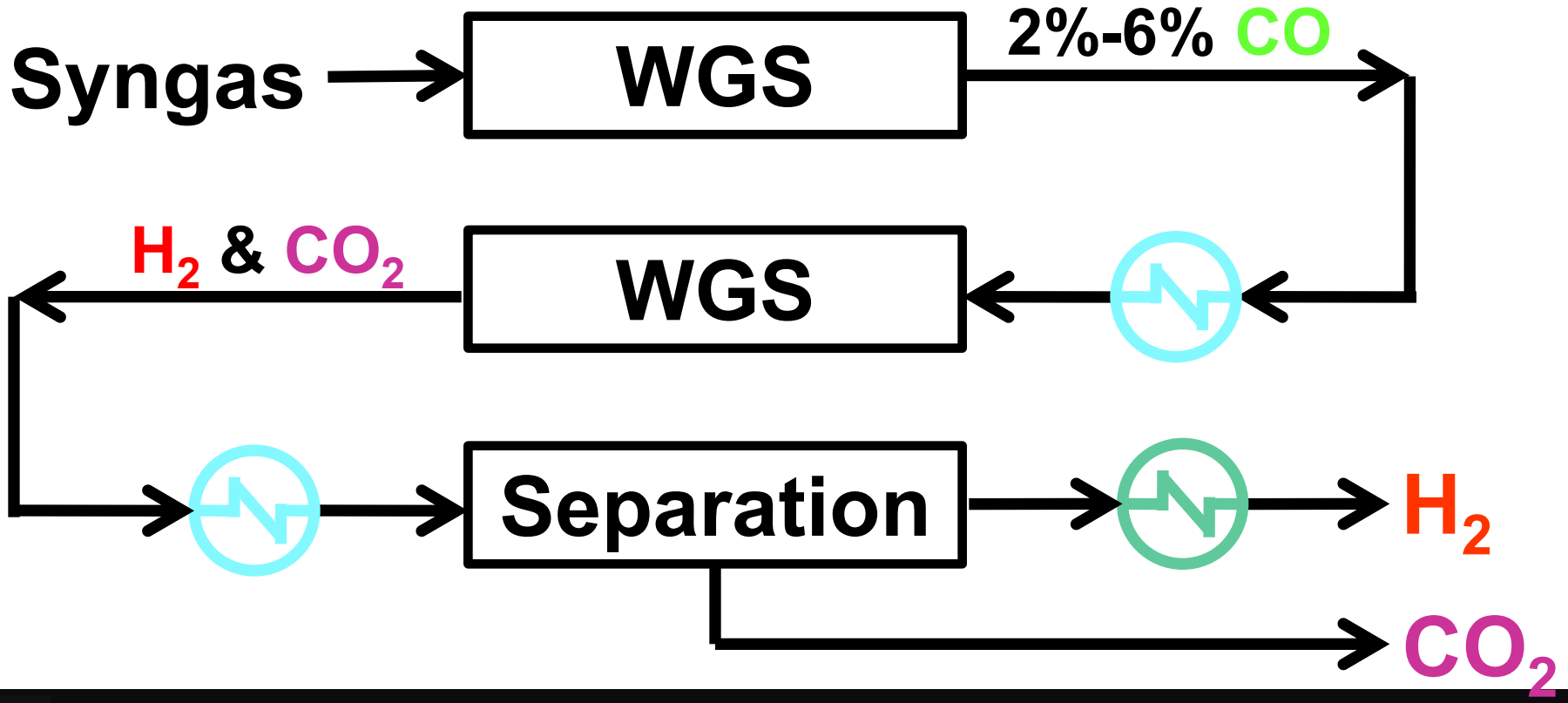
Carbo et al (2009) Int J Greenhouse Gas Ctrl **3** (6) 712

Sorption-Enhanced Water-Gas Shift (SEWGS)

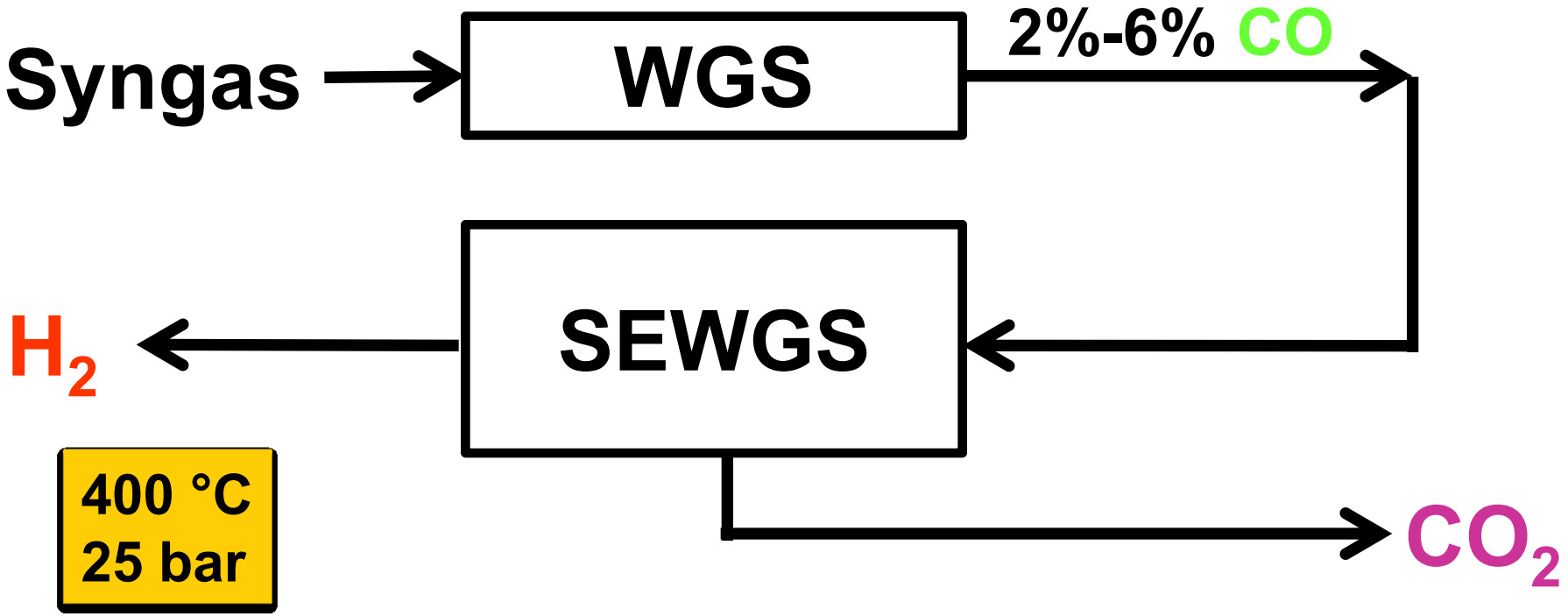


Hot separation
High H_2 recovery
High CO_2/CO rejection

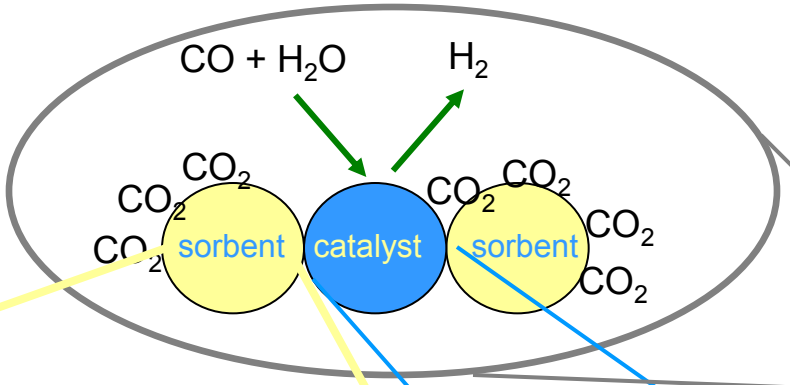
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$



$$CO + H_2O \rightarrow \cancel{CO_2} + H_2$$

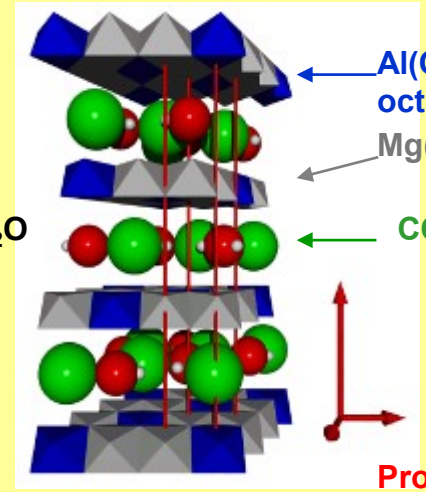


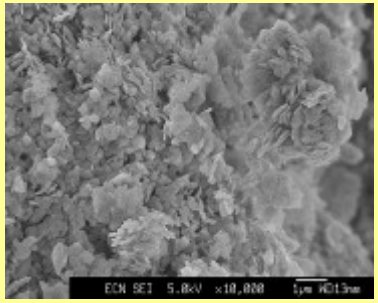
SEWGS principle and Materials



Fe-Cr

$Mg_6Al_2(OH)_{16}CO_3.4H_2O$

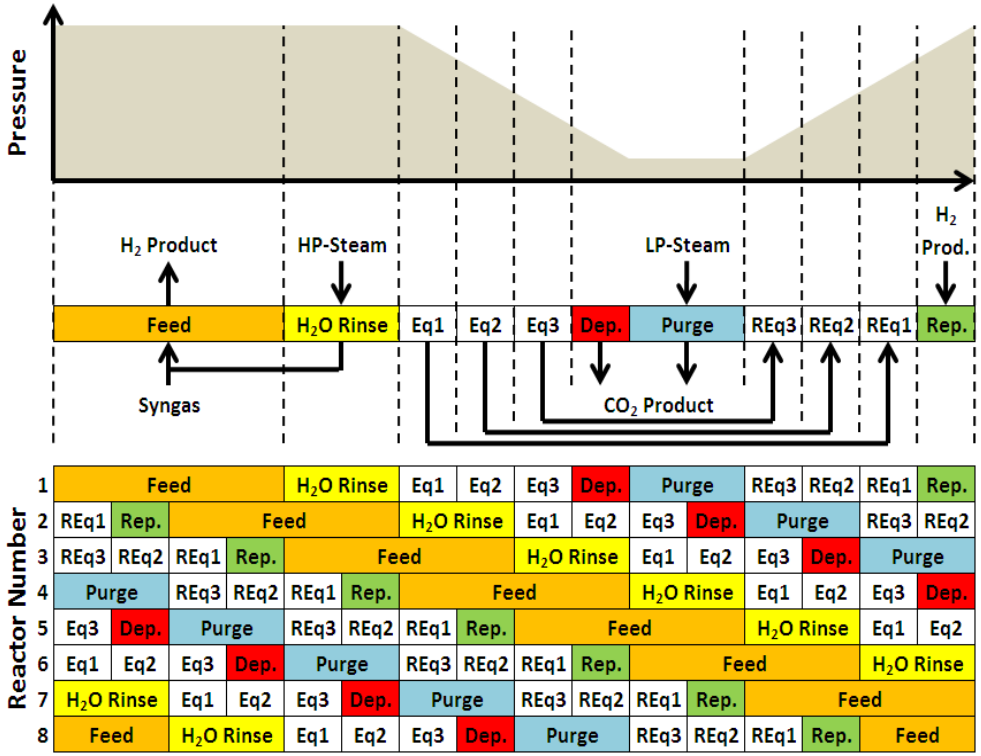


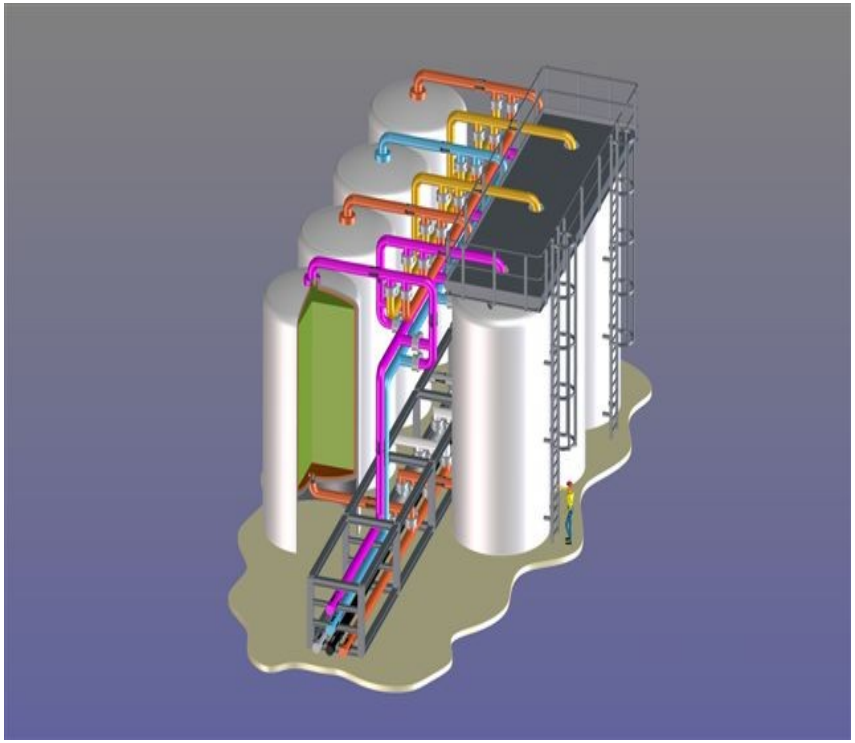


Promoted with K_2CO_3

Hydrotalcite (layered clay)

The SEWGS process; Hot PSA

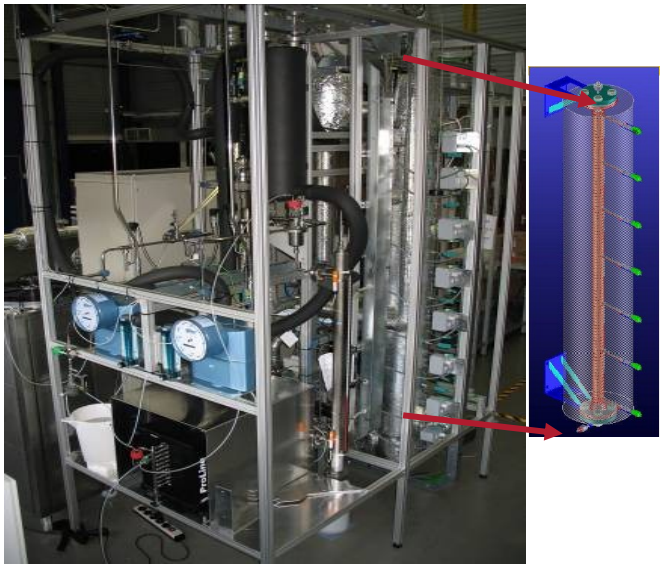




Adsorption – regeneration
cyclic, multi bed process with HTC

350-550°C, 1-30 bar
High pressure, hot hydrogen
Less heating/cooling steps

SEWGS Test Rigs



2 m single column, 38 mm ID
Design conditions:
Tmax: 550°C
Pmax: 31 bara
Feed gases:
CH_4, CO, CO_2, H_2, H_2S, N_2, Steam

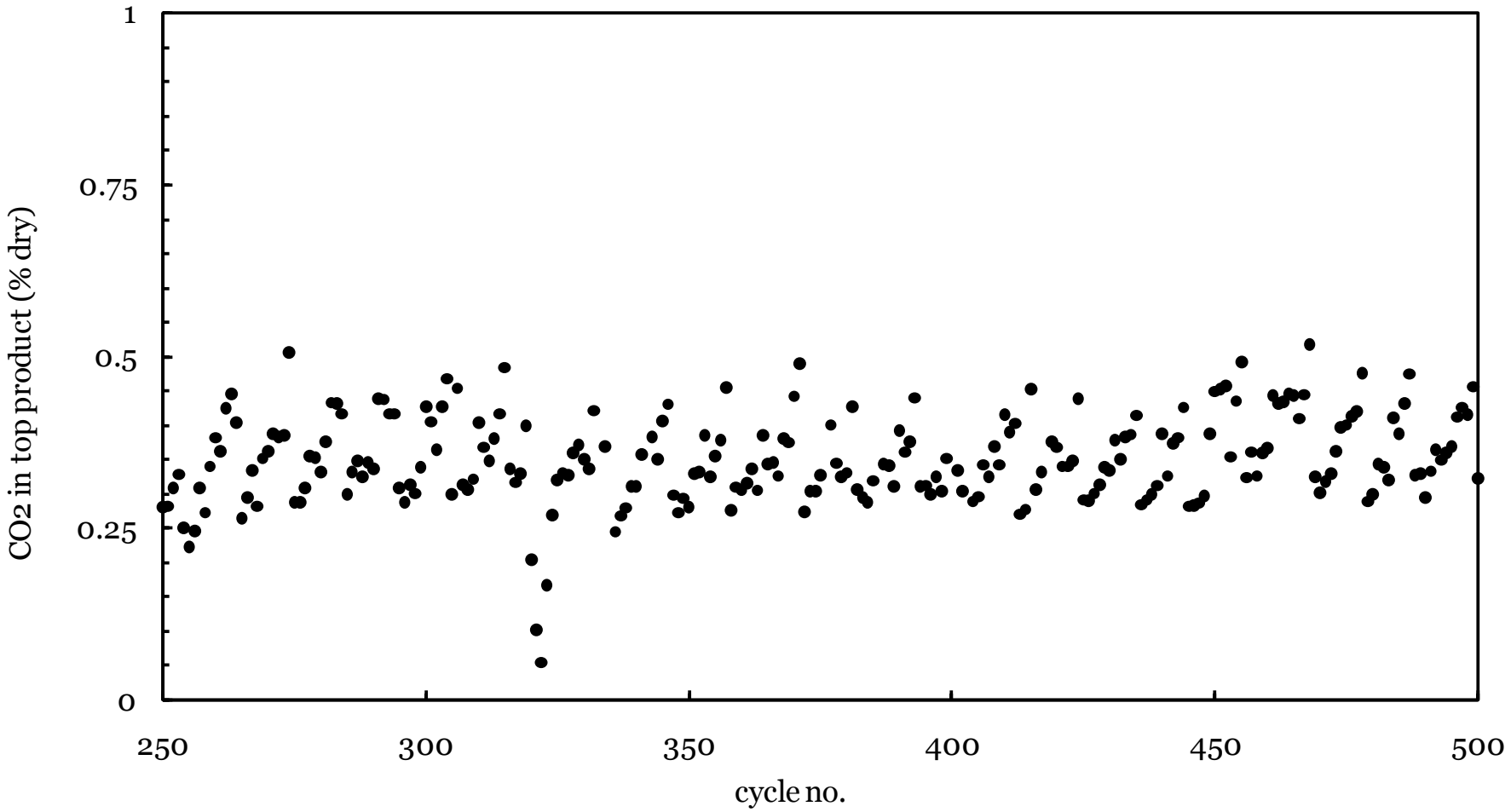
Six, 6 m high,
38 mm ID columns
48 valves

SEWGS: Sorbent development

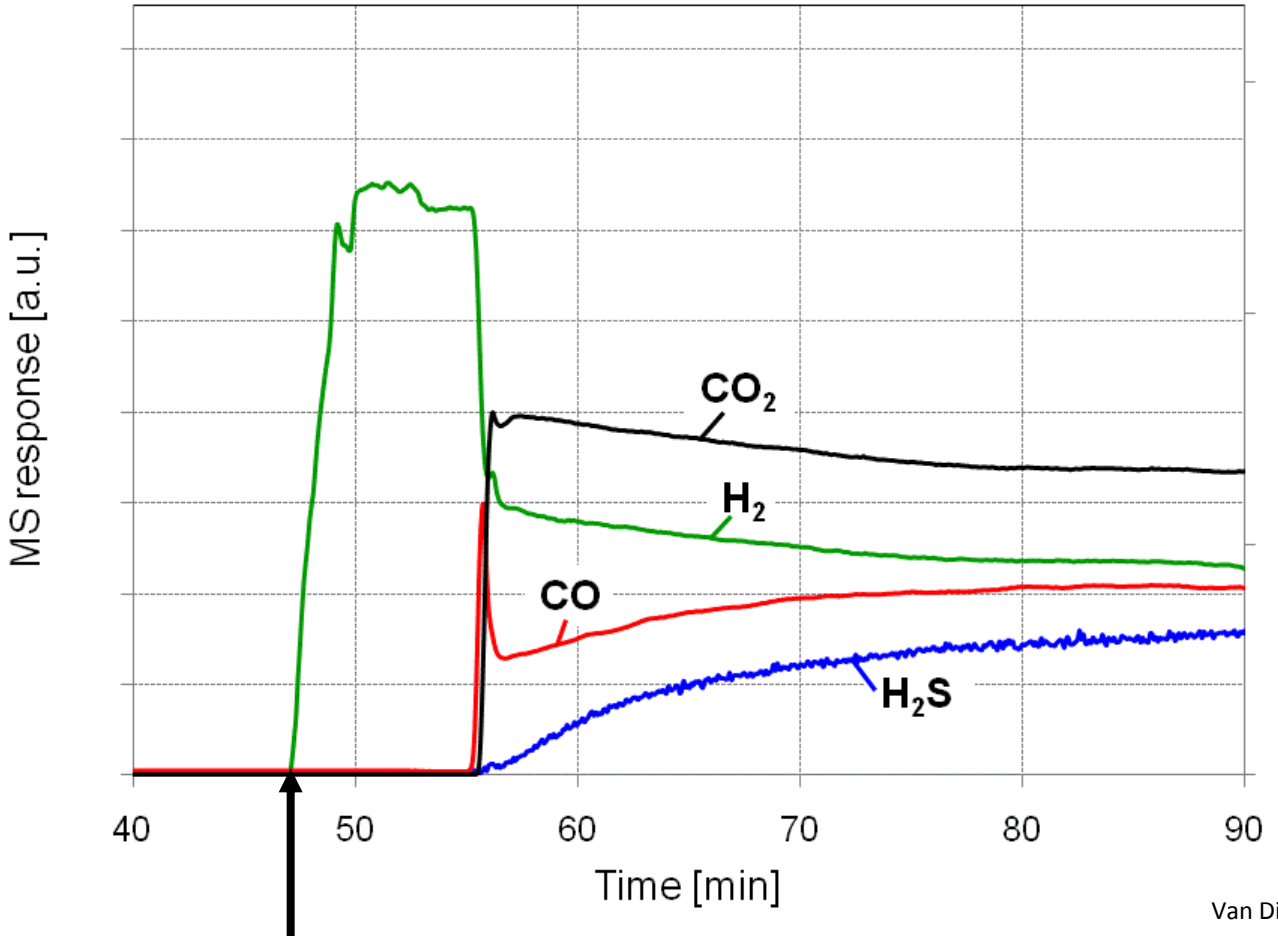
- LT tests showed the stability of the working capacity as well as shift activity of **ALKASORB** during 5000 cycles, at a minimal steam to carbon ratio (2 mole/mole).
- Hence, it was demonstrated that the SEWGS process does **not require a shift catalyst**, which brings substantial economic and technical benefits.
- **ALKASORB** captures also H_2S along with the CO_2 without significant loss of capacity.

SEWGS: Alkasorb sorbent is stable

Van Selow et al (2010) *GHGT-10, Amsterdam*



Sufficient WGS activity before CO_2 breakthrough



400 °C
30 bar

40 % H_2O
17 % CO
17 % H_2
20% CO_2
200 ppm H_2S

Van Dijk et al (2011) *Int J Greenhouse Gas Cntrl* **5** (3) 505

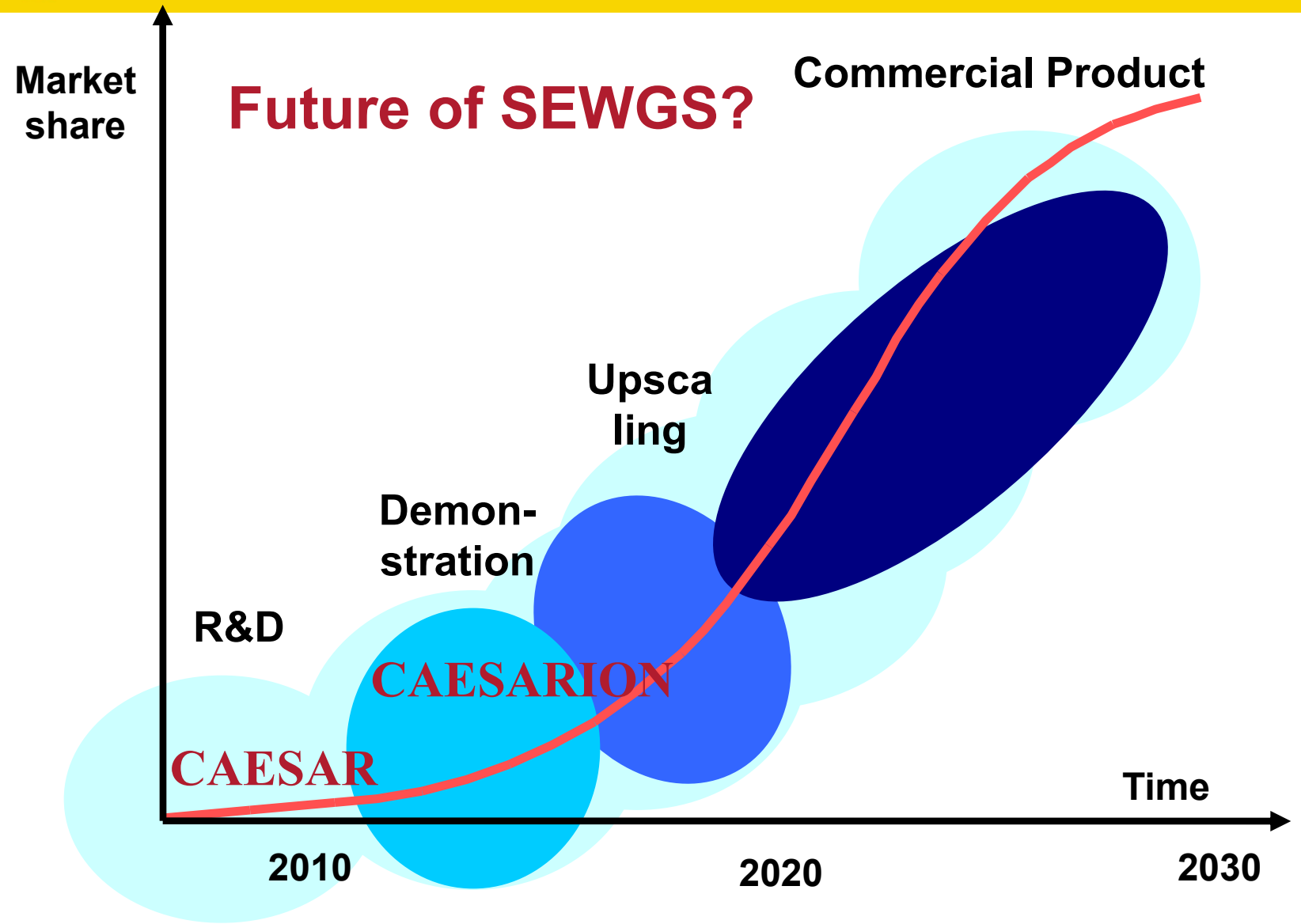
Pre combustion: Effect of SEWGS and a-WGS on efficiency penalty

Losses reduction

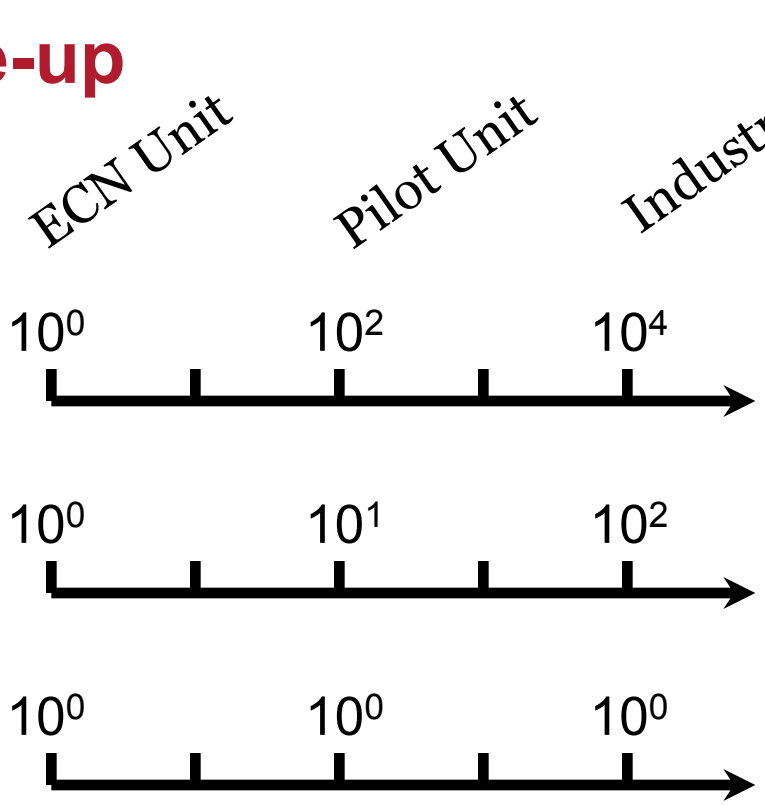
Performance comparison

IGCC, ~400 MW_e		No cap	Selexol	SEWGS
Net Efficiency	%	47.7	**36.5**	**38.4**
CO_2 avoidance	%	-	**87.6**	**98.0**
Specific energy use	GJ/ton_{avoid}	-	**3.7**	**2.6**
Cost of CO_2 avoided,	[€/t_{CO2}]		**40**	**<30**

Gazzani et al. GHGT-10


Market share
Future of SEWGS?
Commercial Product
Upsca ling
Demon- stration
R&D
CAESARION
CAESAR
Time
2010
2020
2030

Scale-up


ECN Unit
Pilot Unit
Industrial Unit
10^0
10^2
10^4
Relative Productivity
10^0
10^1
10^2
Relative Vessel Diameter
10^0
10^0
10^0
Relative Vessel Length,
Superficial Gas Velocity,
Residence Time,
Cycle Time,
Pressure Drop

Conclusions

Physical solvents are attractive for pre-combustion CO_2 capture in IGCC plants

Many Rectisol and Selexol units in operation

Efficiency penalty for CO_2 capture can be reduced

Improved solvents, membrane contacters
Reduction of steam demand for WGS
Process intensification (sorption-enhanced reactor)

Acknowledgements

caesar.ecn.nl

CACHET CO2

CAP TECH

cato

Agentschap NL
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