# Pre-combustion with Physical Absorption

**E.R. van Selow**

**R.W. van den Brink**

*Presented at the 2nd ICEPE,*
*18 November 2011, Frankfurt, Germany*

ECN-L--11-126 November 2011

ECN

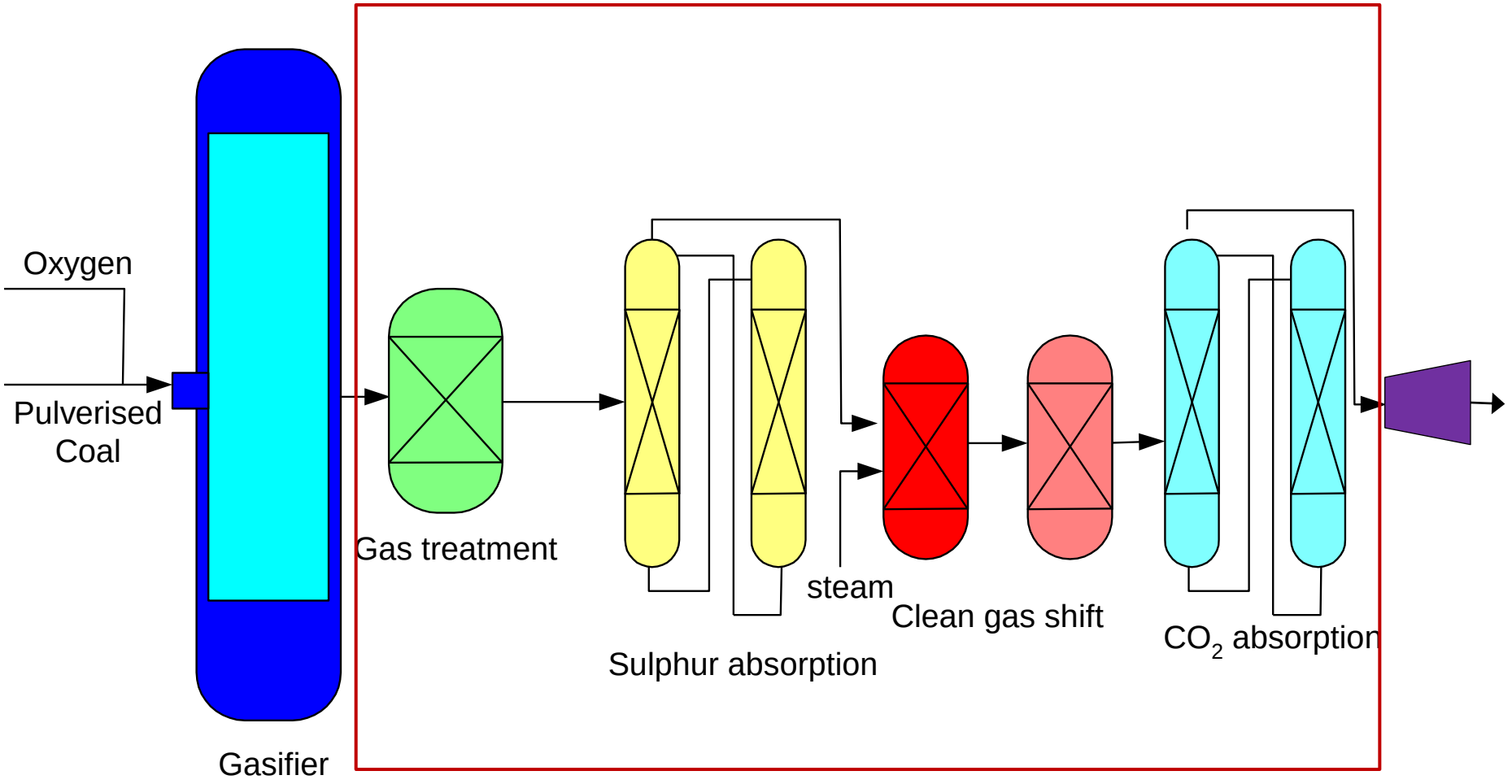
Energy research Centre of the Netherlands

# Pre-combustion with Physical Absorption

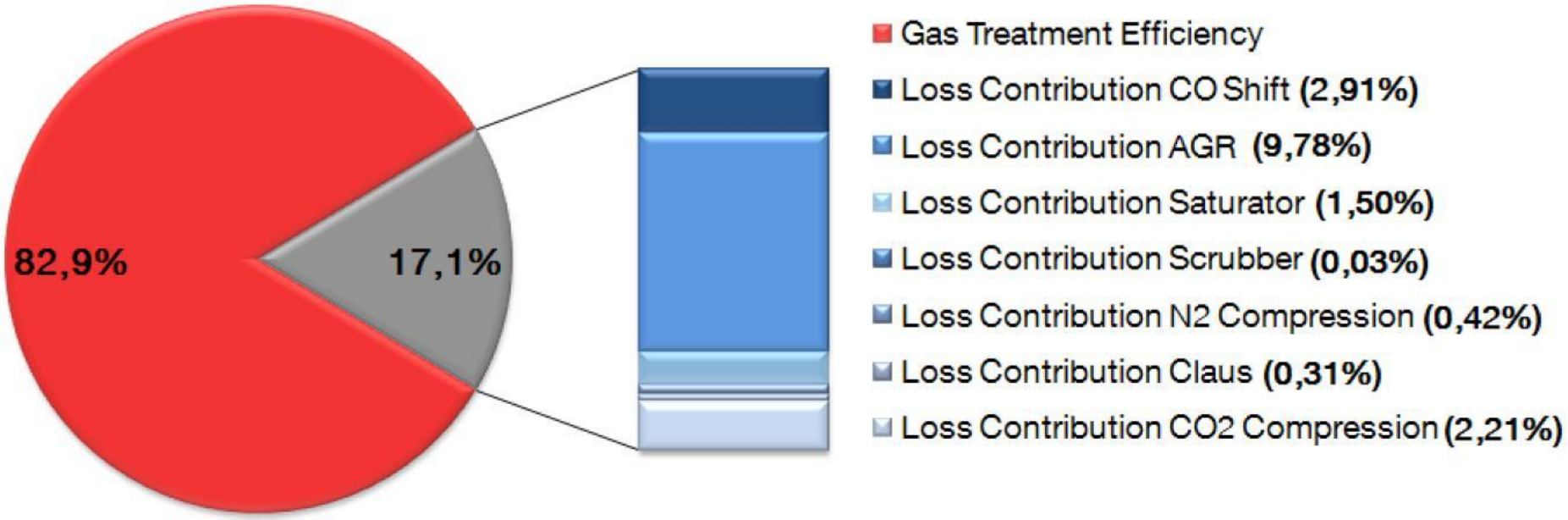
**Ed van Selow, Ruud van den Brink**

*2nd ICEPE, 2011*

# IGCC with carbon removal



# Exergy losses in gas treatment (IGCC with CCS)

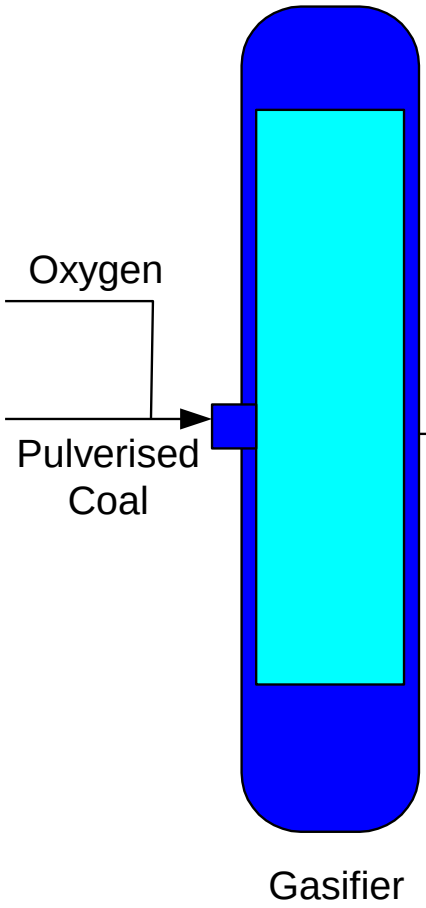



AGR - causes 57% of losses in the subsystem

Kunze et al (2010) 4th Int Freiberg Conf, Dresden

# IGCC with carbon removal

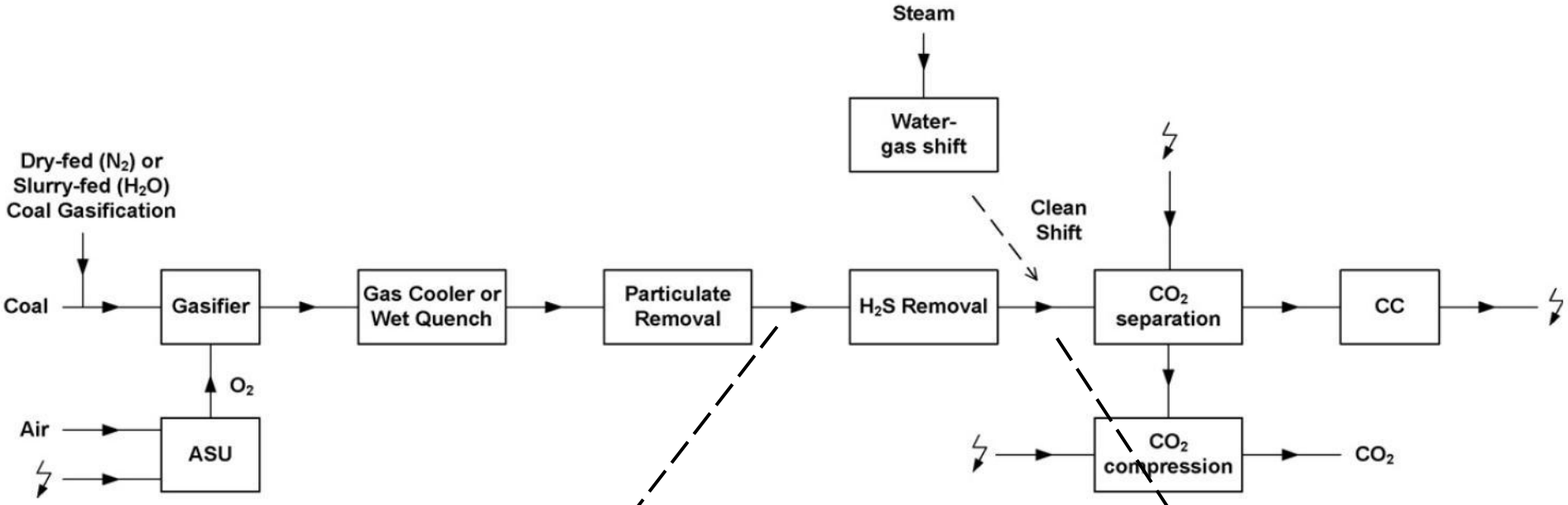
*Gas treatment*




- Sour vs sweet WGS
- Existing sour gas treating technologies
  - Chemical, physical, hybrid absorbents
  - Physical sorbents and processes
- Developments
  - Advanced solvents
  - Advanced shift
  - Low steam sour shift
  - Sour PSA
  - High-temperature gas clean-up
  - Reaction/separation integration: SEWGS
  - Pilot at Buggenum IGCC

# Sour vs sweet WGS

# Sour vs sweet (clean) WGS arrangement

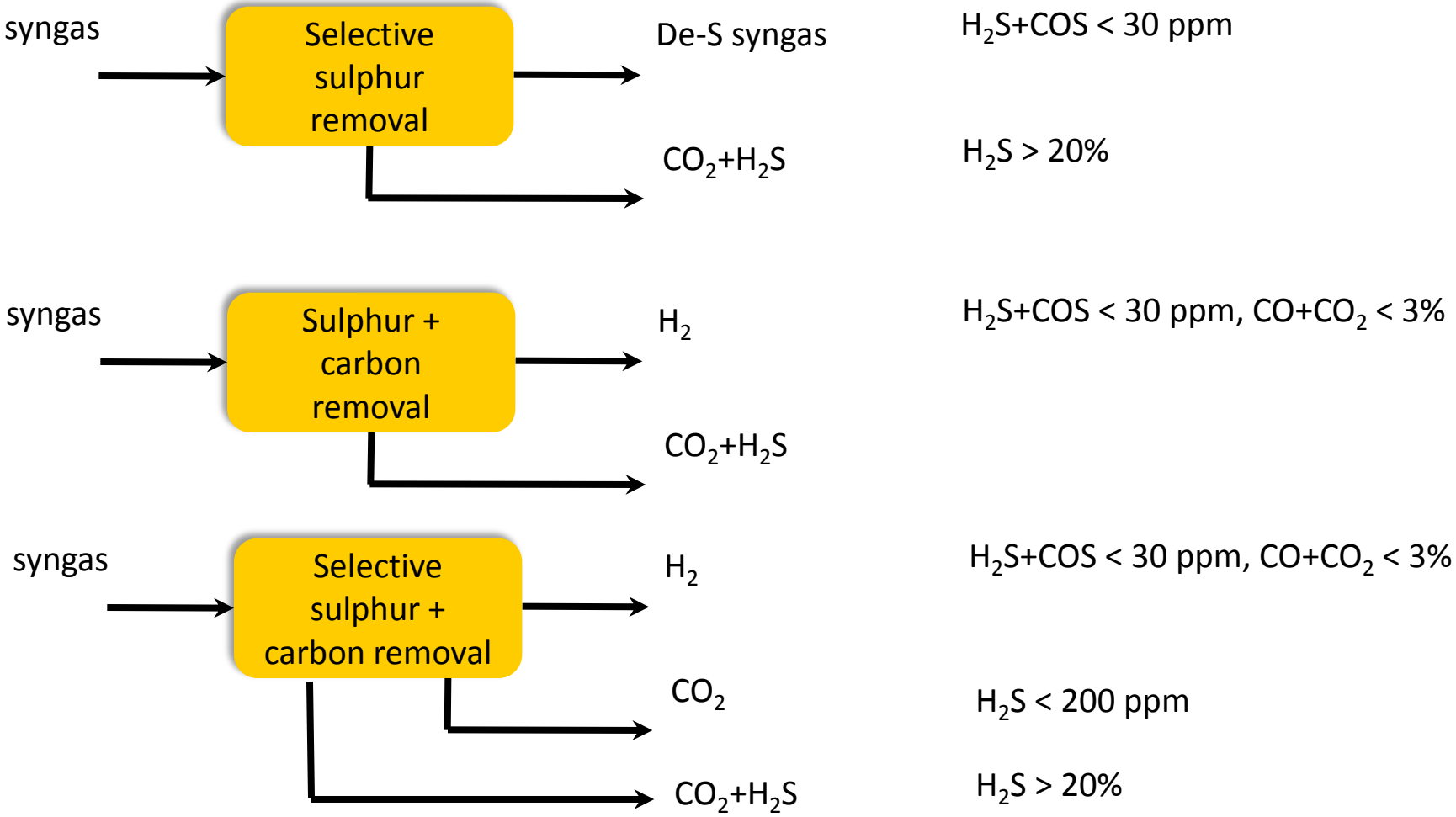



**Sour Shift**
- ✓ Retains steam
- ✓ Hydrolysis COS
- ✓ Operates in a wider temperature range

**Sweet Shift**
- ✓ More selective sulphur removal
- ✓ Smaller reactor
- ✓Cheaper catalyst

# Existing sour gas treating processes

# Gas treatment requirements (example)

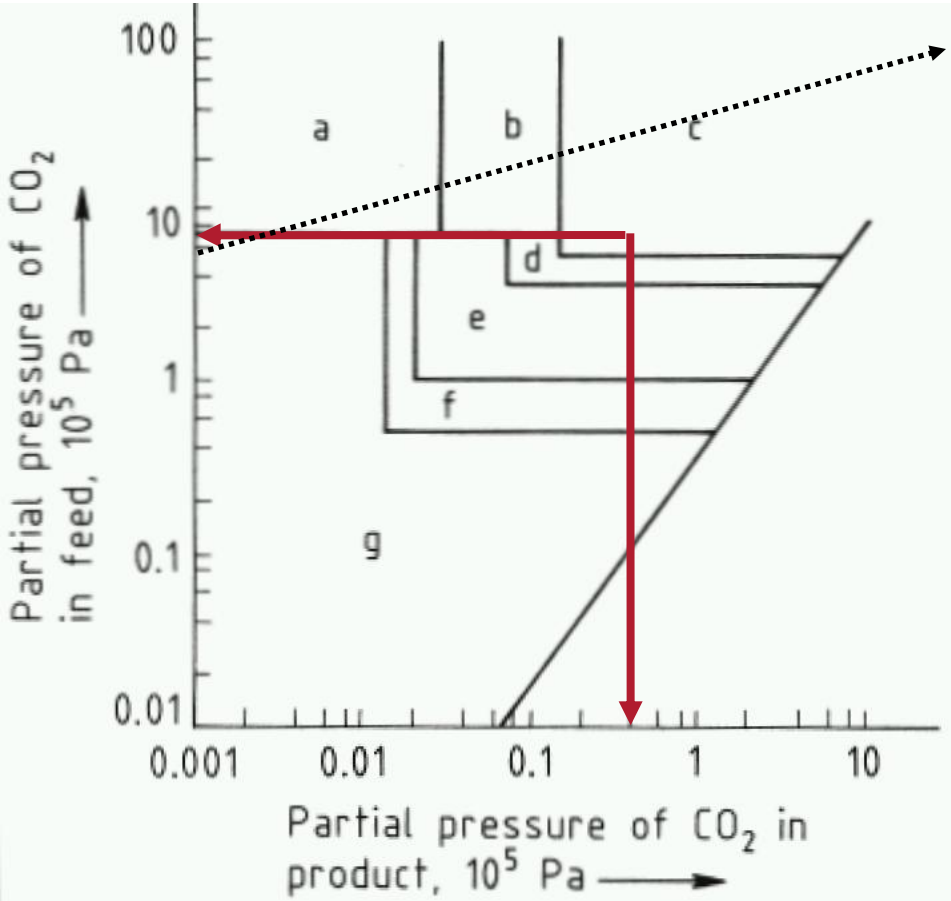


# Selecting the absorbent

| Chemical solvents (amines) | Mixed (hybrid) solvents | Physical solvents |
|---|---|---|
| More efficient at low pressure | | More efficient at high pressure |
| Sulphur removal 98% | Very high sulphur recoveries can be achieved. | Sulphur removal 99%<br>High selectivity for $H_2S$ |
| Higher energy penalty due to steam stripping | | Higher investment costs |
| May form heat-stable salts | | Stable solvent |
| Low coabsorption | | Remove additional impurities such as HCN, $NH_3$<br>Co-adsorption of $H_2$ |

# Selecting the absorption process

Ullmann's Encyclopedia




Trade-off at $p_{CO2}$ ~ 6 bar between solvent loading/recirculation (lean vs. rich) and equipment sizing

Selection of suitable $CO_2$ absorption process:

a) **Physical solvent + amine**

b) **Physical solvent**, **physical solvent + amine** or **activated hot $K_2CO_3$**

c) **Physical solvent**

d) **Physical solvent** or **activated hot $K_2CO_3$**

e) **Activated hot $K_2CO_3$ or concentrated amine**

f) **Activated hot $K_2CO_3$ or amine**

g) **Amine**

| | | 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

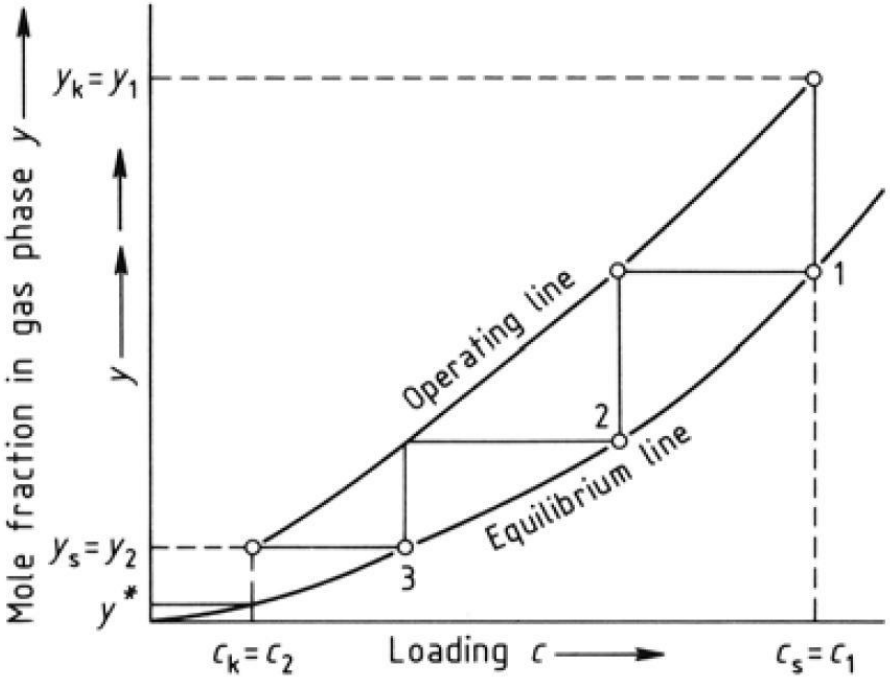
| Gas | Selexol | Fluor solvent | Purisol | Methanol |
|---|---|---|---|---|
| $H_2$ | 0.047 | 0.027 | 0.02 | - |
| CO | 0.10 | 0.072 | 0.075 | - |
| $C_1$ | 0.24 | 0.13 | 0.26 | - |
| $C_2$ | 1.52 | 0.58 | 1.36 | - |
| $CO_2$ | 3.63 | 3.41 | 3.57 | 15 |
| $C_3$ | 3.7 | 1.74 | 3.82 | - |
| COS | 8.46 | 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)

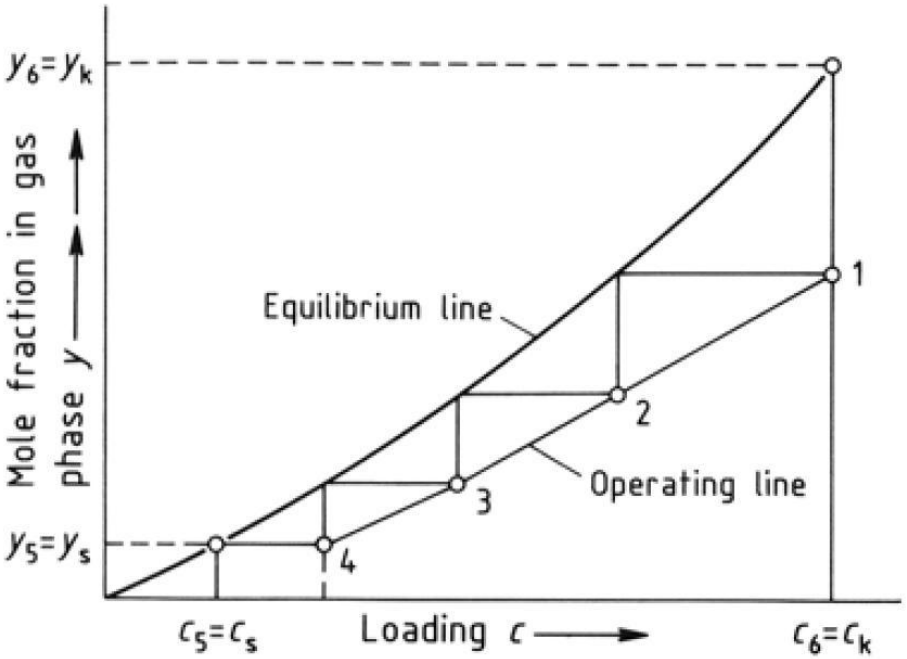
# Comparing Selexol and Rectisol processes

| | Selexol | Rectisol |
|---|---|---|
| $H_2S$ selectivity | 9 | 6 |
| $H_2S$+COS removal | | < 0.1 ppm $H_2S$ + COS<br>Few ppm $CO_2$ |
| Temperature | -5 .. 175 °C | -60 .. -15 °C |
| OPEX, CAPEX | | Higher OPEX and CAPEX: complex scheme and need to refrigerate |
| Other | COS hydrolysis needed | High vapor losses |

# Absorber/desorber column design

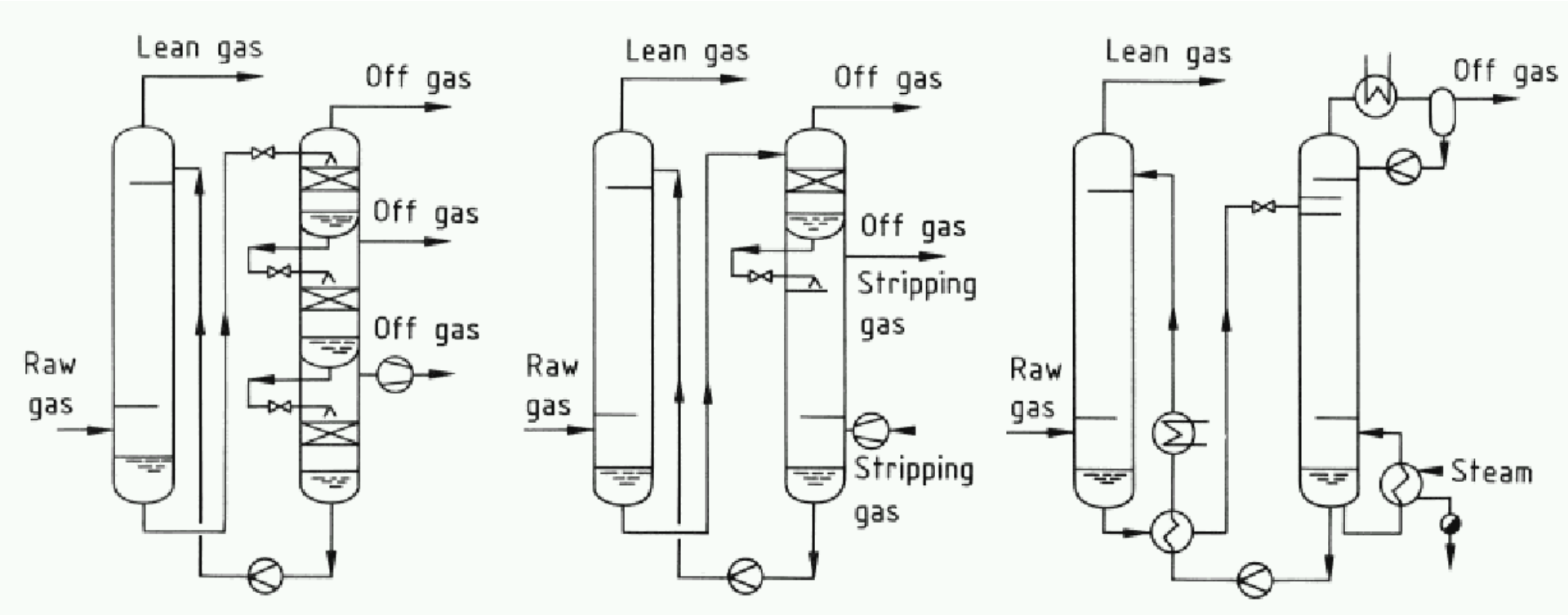



Absorption



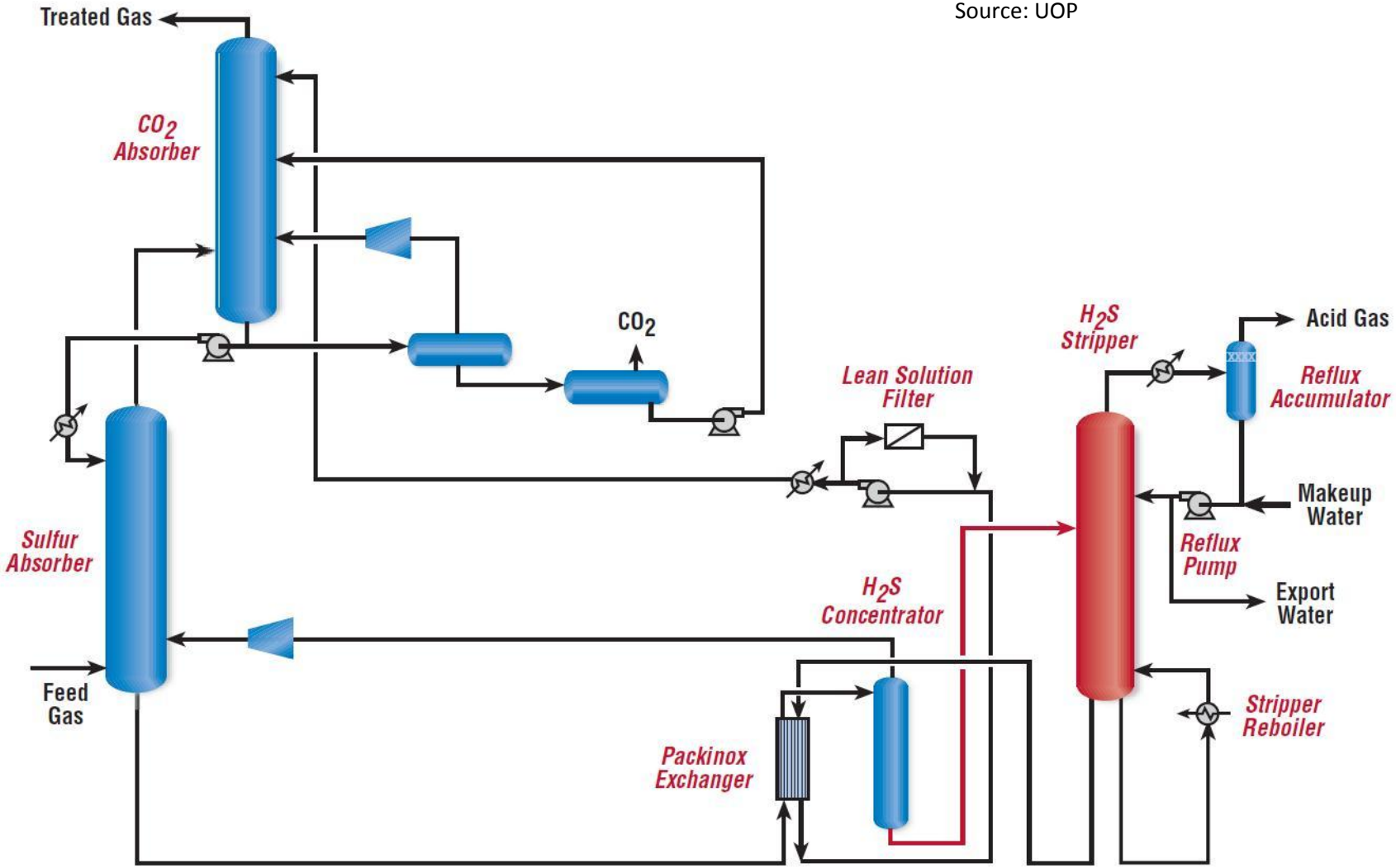

Stripping

# Regeneration of solvents

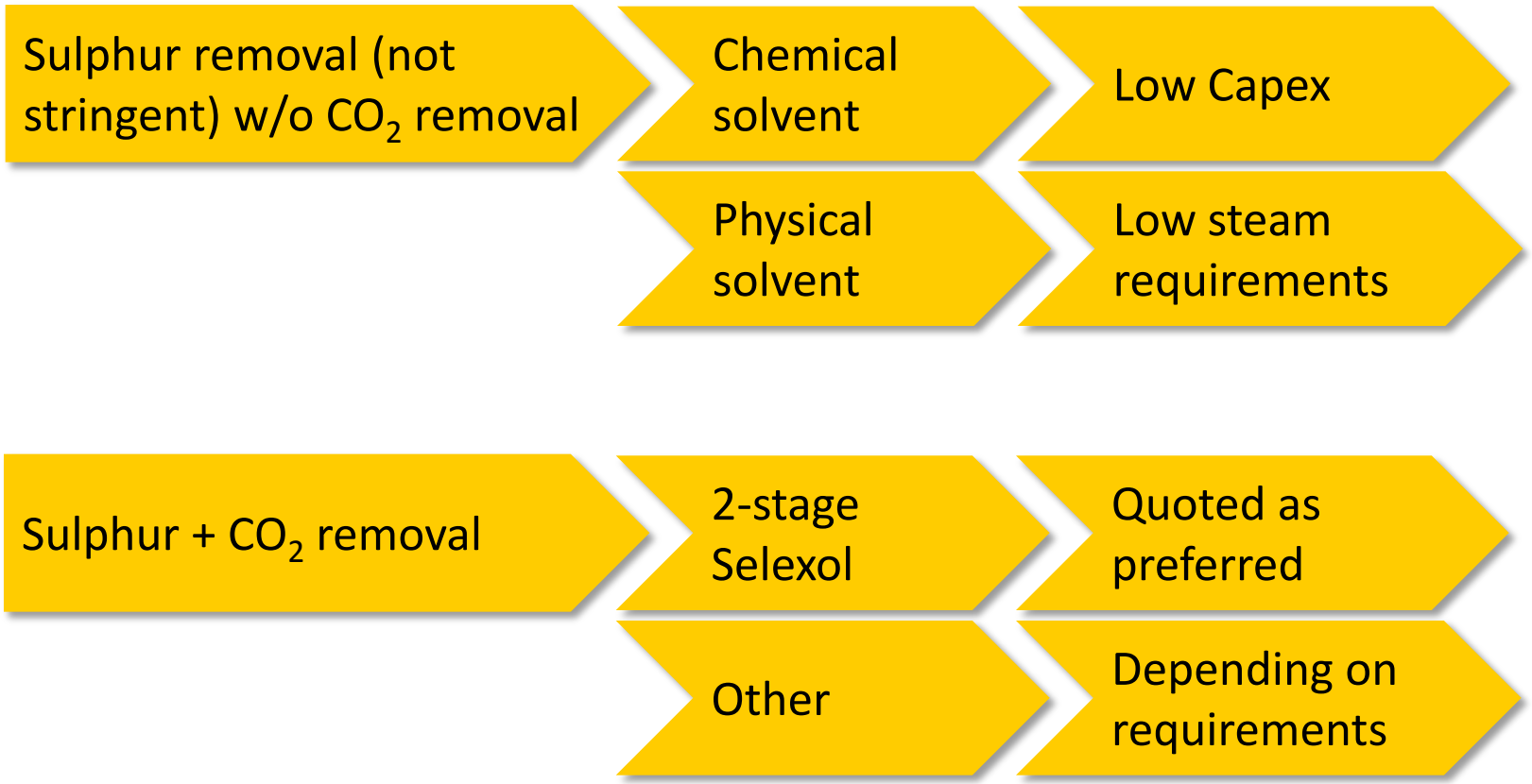



*Flashing* *Stripping* *Reboiling*

Source: UOP


Treated Gas
$CO_2$ Absorber
$CO_2$
$H_2S$ Stripper
Acid Gas
Lean Solution Filter
Reflux Accumulator
Makeup Water
Sulfur Absorber
Reflux Pump
$H_2S$ Concentrator
Export Water
Feed Gas
Stripper Reboiler
Packinox Exchanger

# Selecting the absorption process in IGCC



# IGCC/CCS studies

**NETL/Parsons**
**2002**. Evaluation of Fossil Fuel Power Plants with $CO_2$ Recovery.
**2007**. Cost and Performance Baseline for Fossil Energy Plants. DOE/NETL-2007/1281.

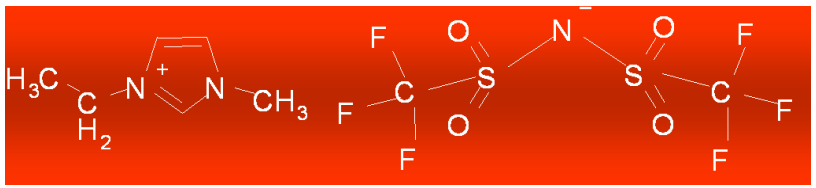
**Foster Wheeler**
**2003**. Potential for improvement in gasification combined cycle power generation with $CO_2$ capture. IEA report No. PH4/19, 2003.
**2007**. Co-production of hydrogen and electricity by coal gasification with $CO_2$ capture. IEA Greenhouse Gas Program report 2007-13.

**Politecnico di Milano / Alstom UK**
**2011**. European best practice guidelines for assessment of $CO_2$ capture technologies.

# New Developments

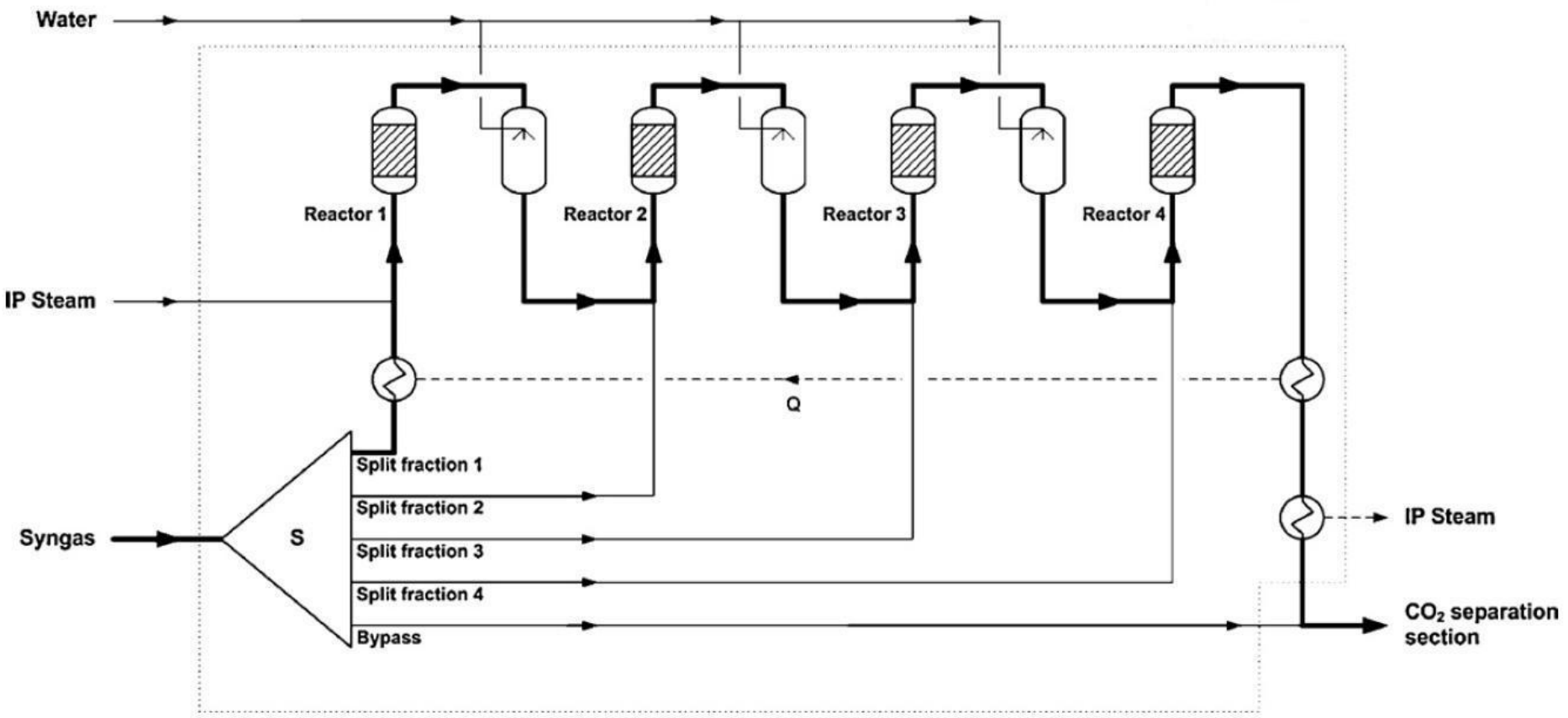
# Improvements in $CO_2$ solvent process

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

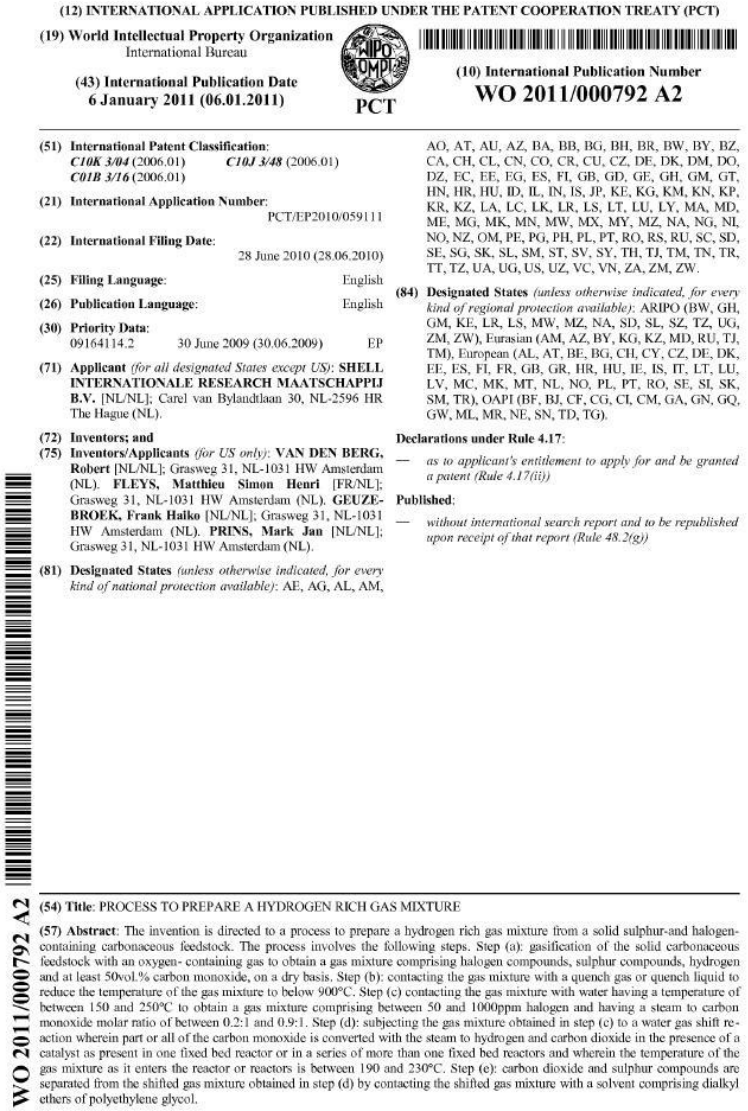


# Advanced Shift (Sweet/Sour)

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



# Low-Steam Sour Shift



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
6 January 2011 (06.01.2011)

PCT

(10) International Publication Number
WO 2011/000792 A2

(51) International Patent Classification:
*C10K 3/04* (2006.01) *C10J 3/48* (2006.01)
*C01B 3/16* (2006.01)

(21) International Application Number:
PCT/EP2010/059111

(22) International Filing Date:
28 June 2010 (28.06.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09164114.2 30 June 2009 (30.06.2009) EP

(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **VAN DEN BERG, Robert** [NL/NL]; Grasweg 31, NL-1031 HW Amsterdam (NL). **FLEYS, Matthieu Simon Henri** [FR/NL]; Grasweg 31, NL-1031 HW Amsterdam (NL). **GEUZEBROEK, Frank Haiko** [NL/NL]; Grasweg 31, NL-1031 HW Amsterdam (NL). **PRINS, Mark Jan** [NL/NL]; Grasweg 31, NL-1031 HW Amsterdam (NL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17**:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

**Published**:

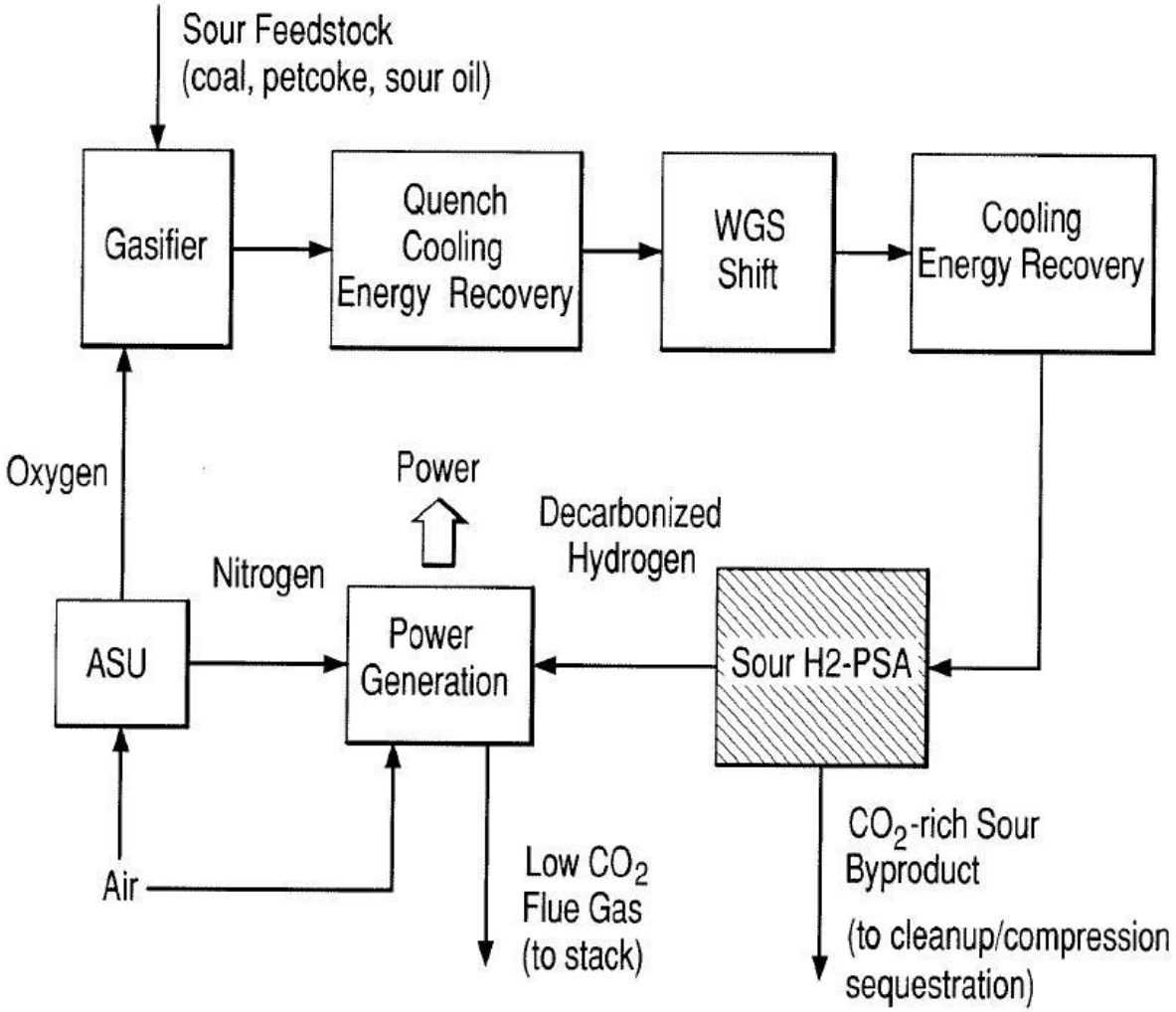
— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

WO 2011/000792 A2

(54) Title: PROCESS TO PREPARE A HYDROGEN RICH GAS MIXTURE

(57) Abstract: The invention is directed to a process to prepare a hydrogen rich gas mixture from a solid sulphur-and halogen-containing carbonaceous feedstock. The process involves the following steps. Step (a): gasification of the solid carbonaceous feedstock with an oxygen- containing gas to obtain a gas mixture comprising halogen compounds, sulphur compounds, hydrogen and at least 50vol.% carbon monoxide, on a dry basis. Step (b): contacting the gas mixture with a quench gas or quench liquid to reduce the temperature of the gas mixture to below 900°C. Step (c) contacting the gas mixture with water having a temperature of between 150 and 250°C to obtain a gas mixture comprising between 50 and 1000ppm halogen and having a steam to carbon monoxide molar ratio of between 0.2:1 and 0.9:1. Step (d): subjecting the gas mixture obtained in step (c) to a water gas shift reaction wherein part or all of the carbon monoxide is converted with the steam to hydrogen and carbon dioxide in the presence of a catalyst as present in one fixed bed reactor or in a series of more than one fixed bed reactors and wherein the temperature of the gas mixture as it enters the reactor or reactors is between 190 and 230°C. Step (e): carbon dioxide and sulphur compounds are separated from the shifted gas mixture obtained in step (d) by contacting the shifted gas mixture with a solvent comprising dialkyl ethers of polyethylene glycol.

# Sour $H_2$ PSA




US2010.011955

# Drivers for high-temperature gas clean-up

The higher process efficiency without syngas cooling and removal of water from the syngas: +5.2%-points*.

The elimination of sour water treating.

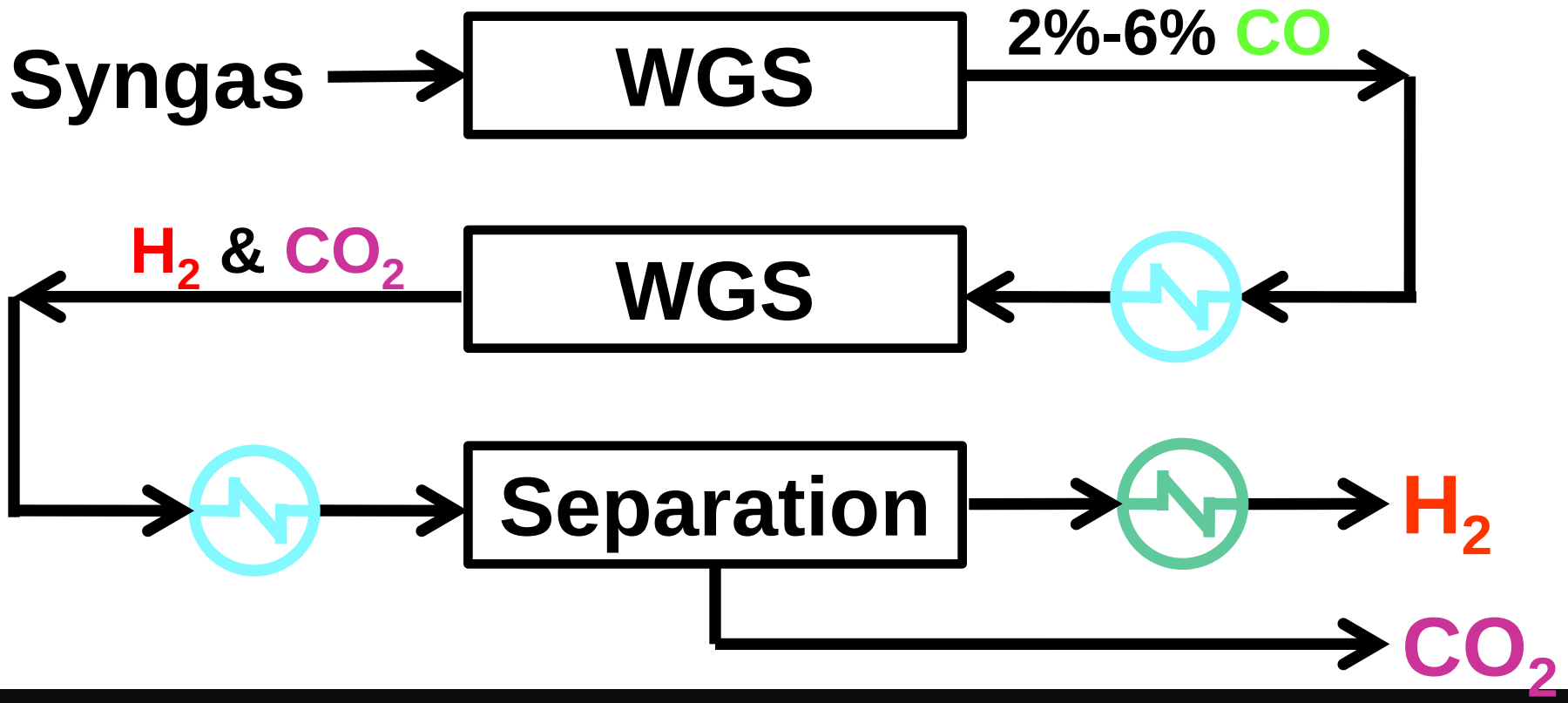
The elimination of the *black mud* produced in wet scrubbing of particulates from the syngas.

The potential related Capex and Opex savings.

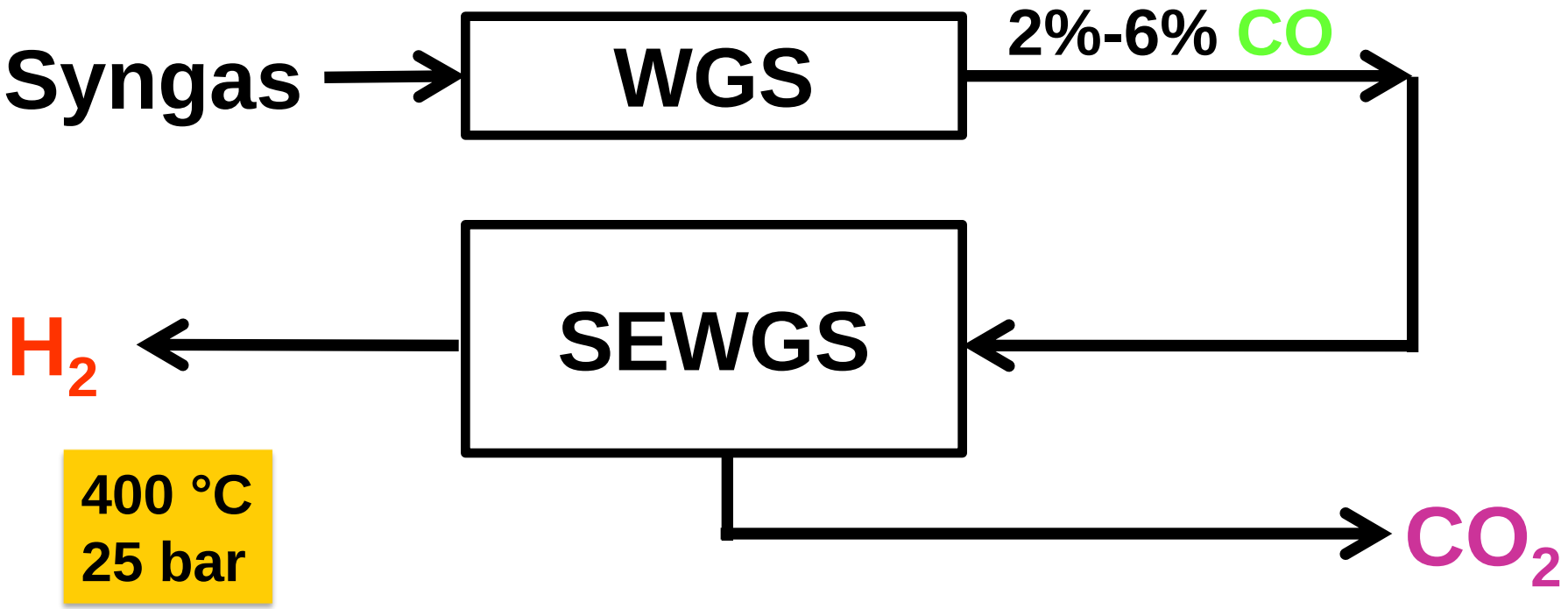
The viability of air-blown gasifiers.

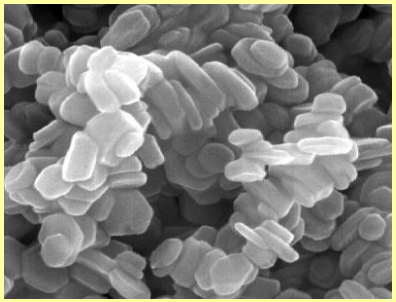
* Exergetic efficiency. Kunze et al. Energy 36 (2011) 1480

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



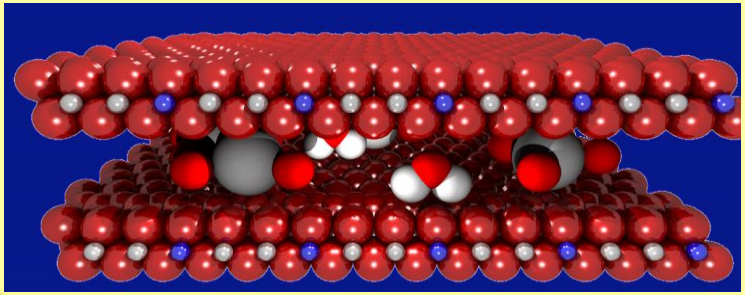
$$CO + H_2O \rightarrow \cancel{CO_2} + H_2$$



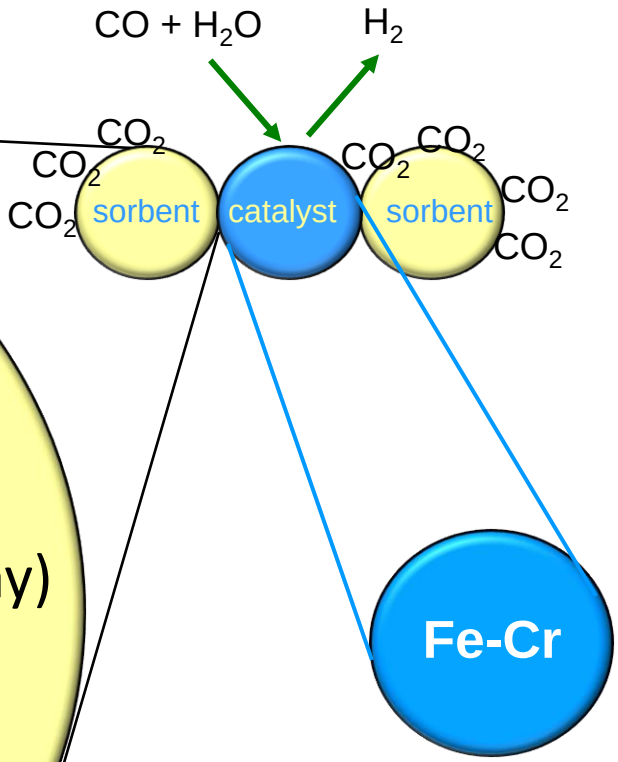


*Meis et al. (2008)*

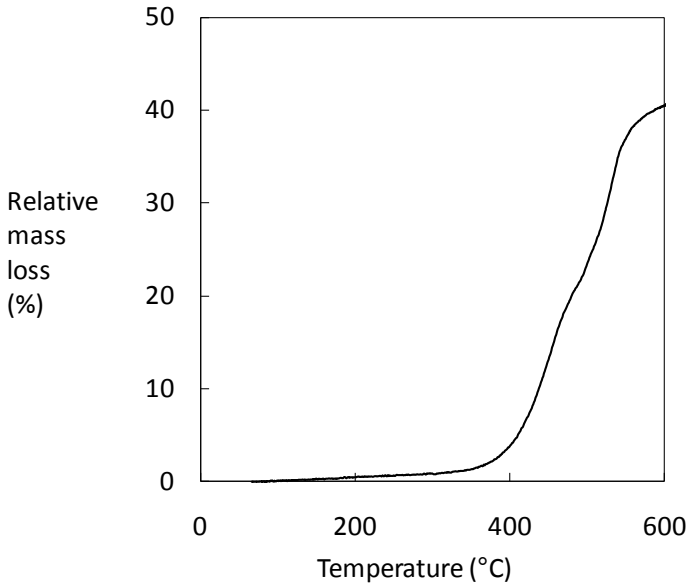
K-promoted Hydrotalcite (layered clay)

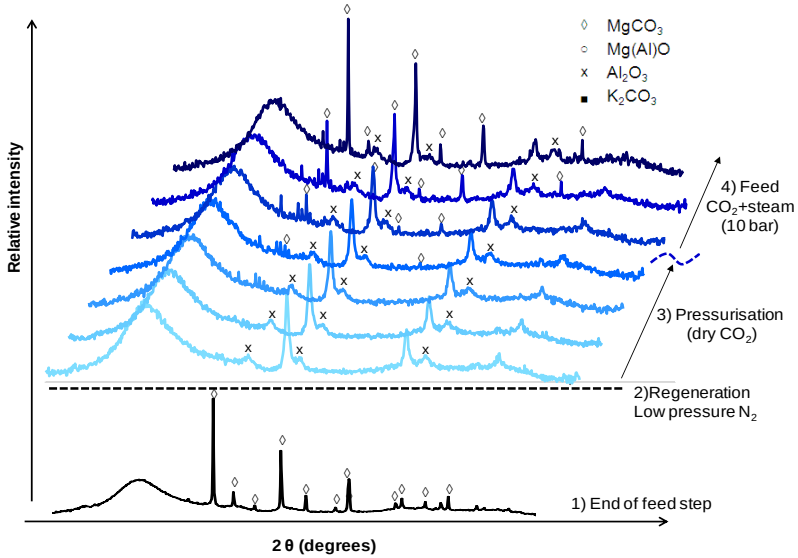


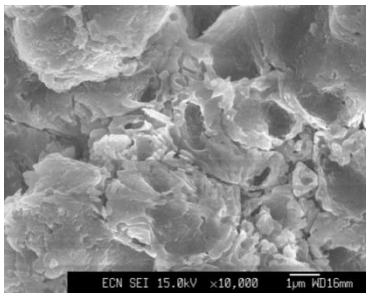
$Mg_6Al_2(OH)_{16}CO_3.4H_2O$

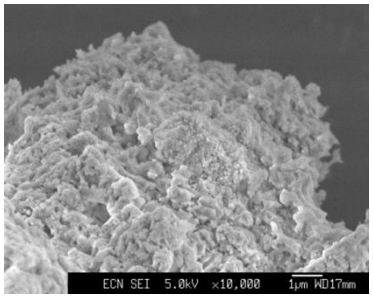


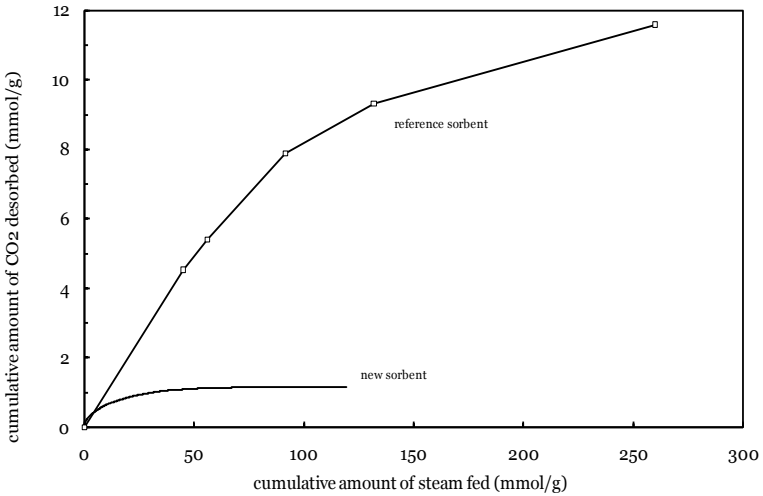
# Formation of $MgCO_3$

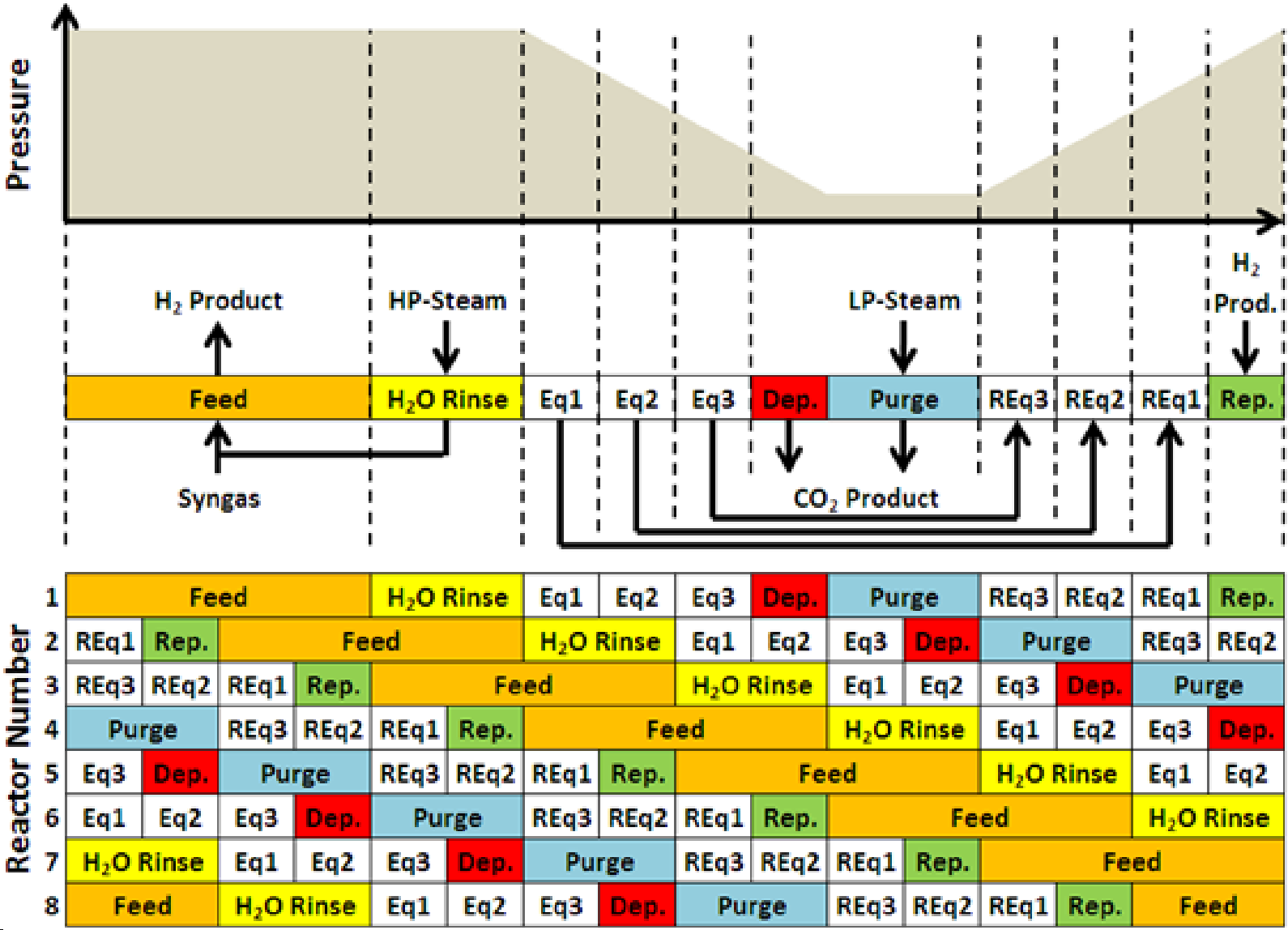


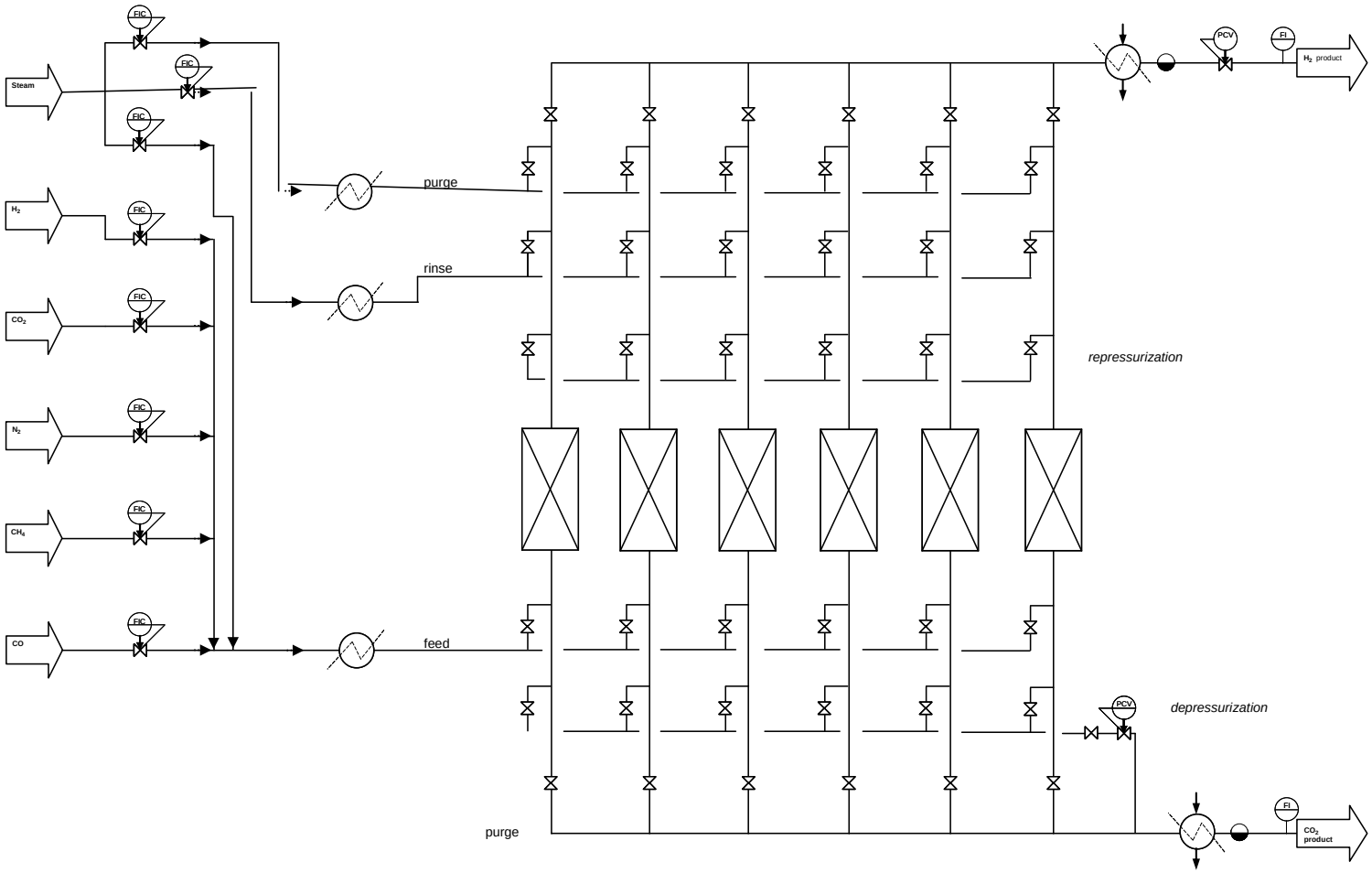



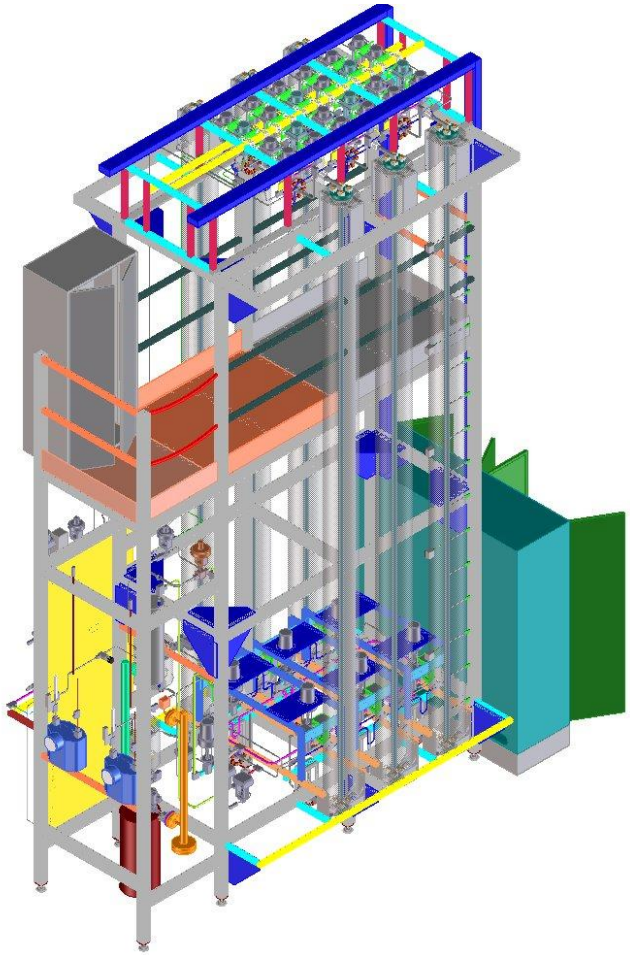




Pressure
H2 Product
HP-Steam
LP-Steam
H2 Prod.
Feed
H2O Rinse
Eq1
Eq2
Eq3
Dep.
Purge
REq3
REq2
REq1
Rep.
Syngas
CO2 Product
Reactor Number
1 Feed H2O Rinse Eq1 Eq2 Eq3 Dep. Purge REq3 REq2 REq1 Rep.
2 REq1 Rep. Feed H2O Rinse Eq1 Eq2 Eq3 Dep. Purge REq3 REq2
3 REq3 REq2 REq1 Rep. Feed H2O Rinse Eq1 Eq2 Eq3 Dep. Purge
4 Purge REq3 REq2 REq1 Rep. Feed H2O Rinse Eq1 Eq2 Eq3 Dep.
5 Eq3 Dep. Purge REq3 REq2 REq1 Rep. Feed H2O Rinse Eq1 Eq2
6 Eq1 Eq2 Eq3 Dep. Purge REq3 REq2 REq1 Rep. Feed H2O Rinse
7 H2O Rinse Eq1 Eq2 Eq3 Dep. Purge REq3 REq2 REq1 Rep. Feed
8 Feed H2O Rinse Eq1 Eq2 Eq3 Dep. Purge REq3 REq2 REq1 Rep. Feed

# SEWGS multi-column unit at ECN

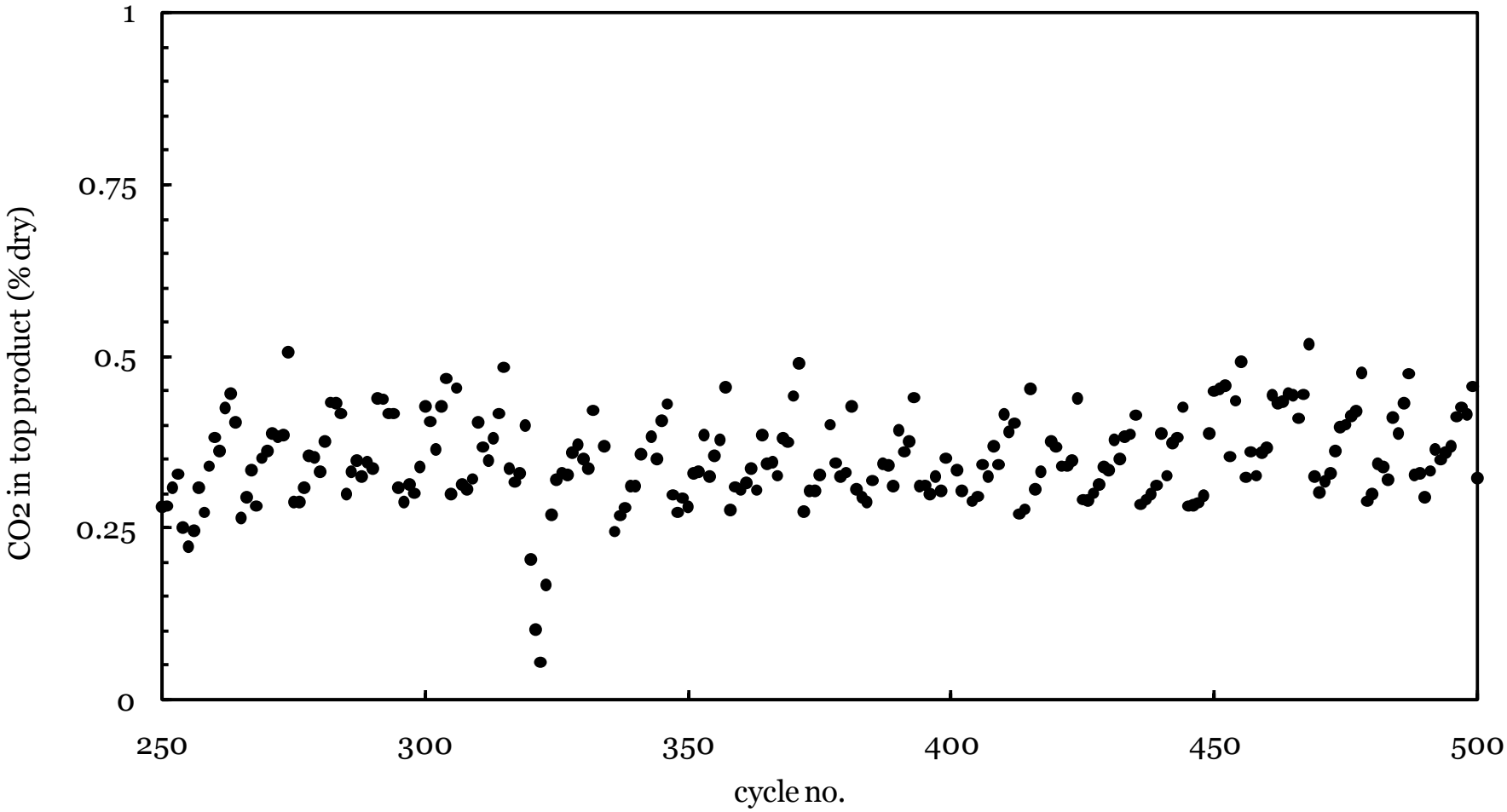


# SEWGS process development unit at ECN



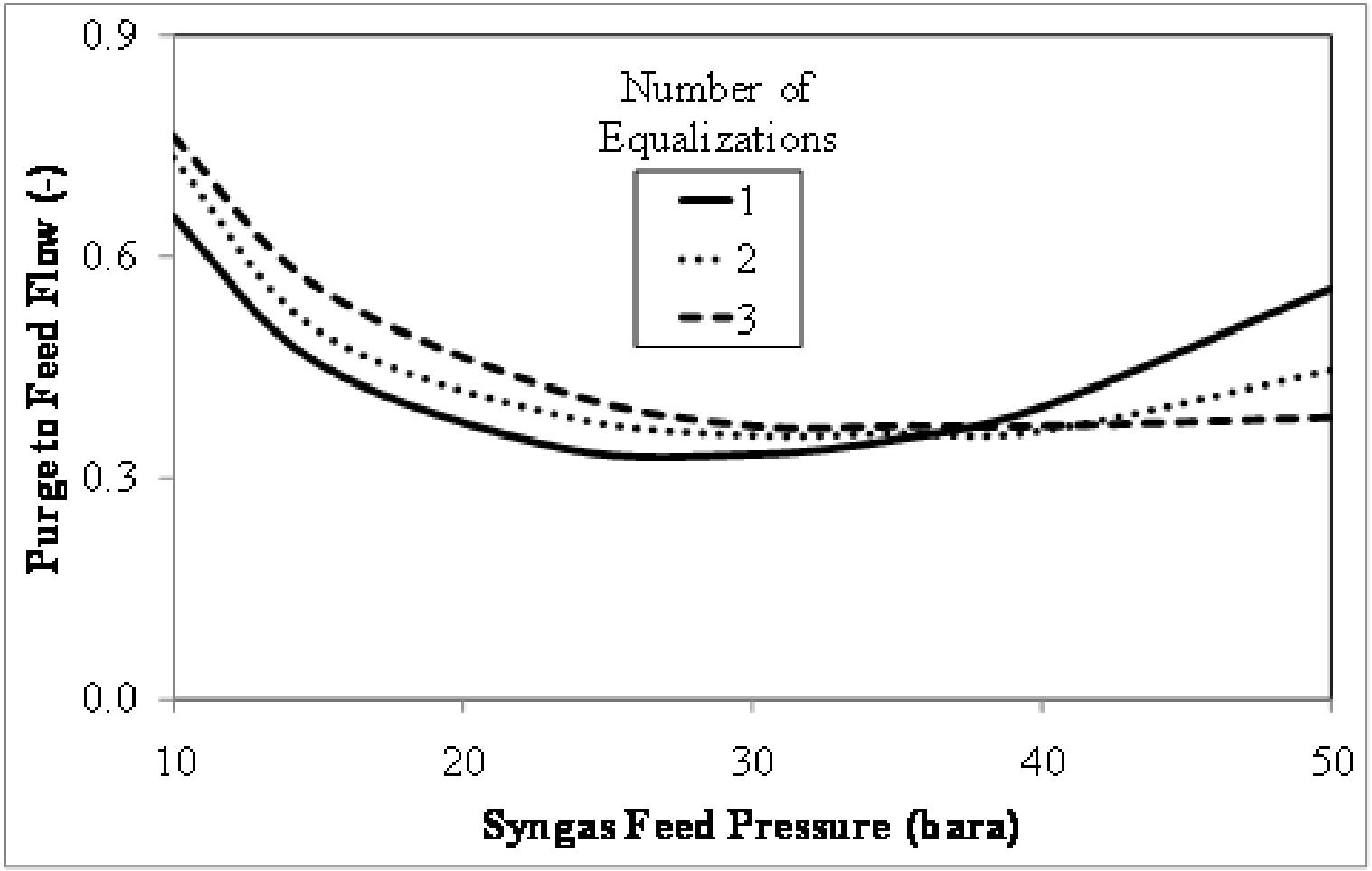
# Alkasorb sorbent is stable

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



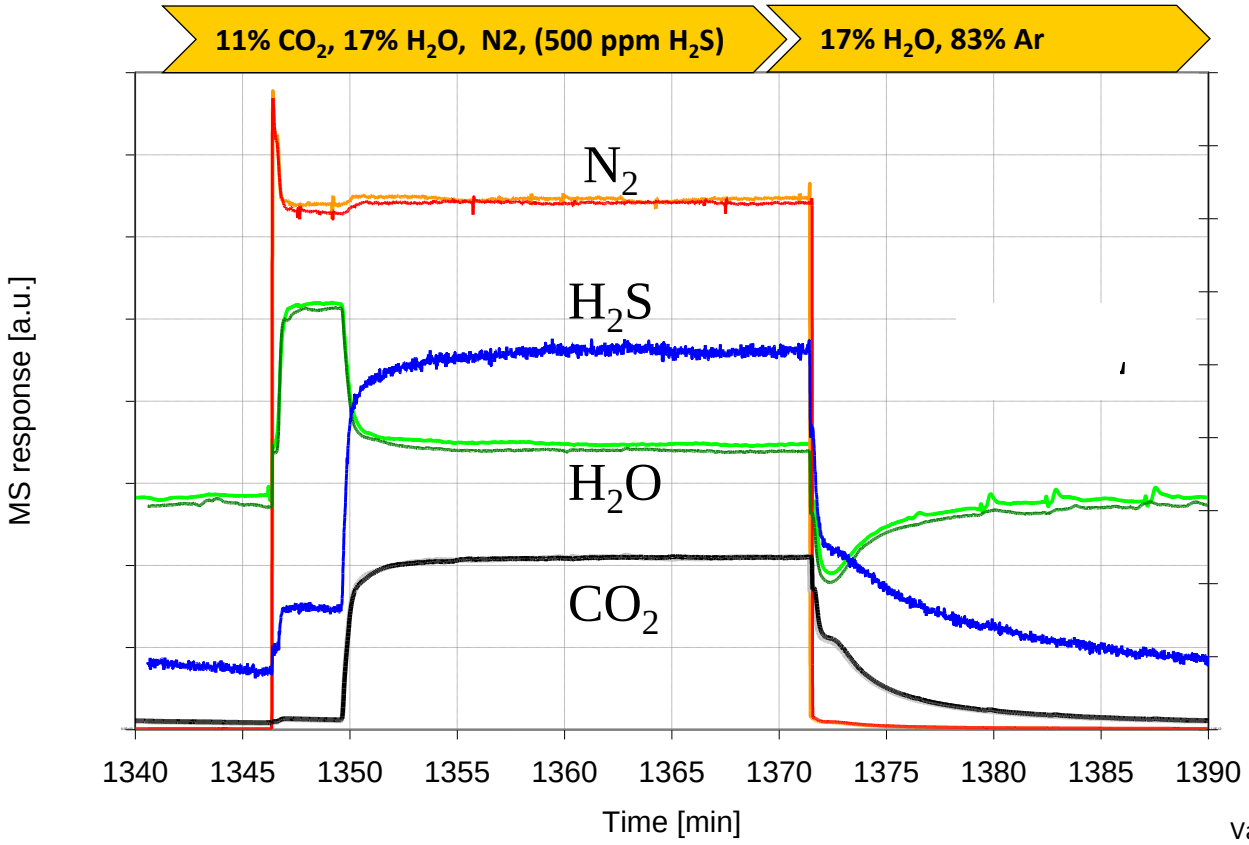
# Effect of feed pressure

Wright et al (2010) *GHGT-10, Amsterdam*



# Co-capture of $H_2S$

$H_2S$ does not change $CO_2$ sorption capacity or kinetics

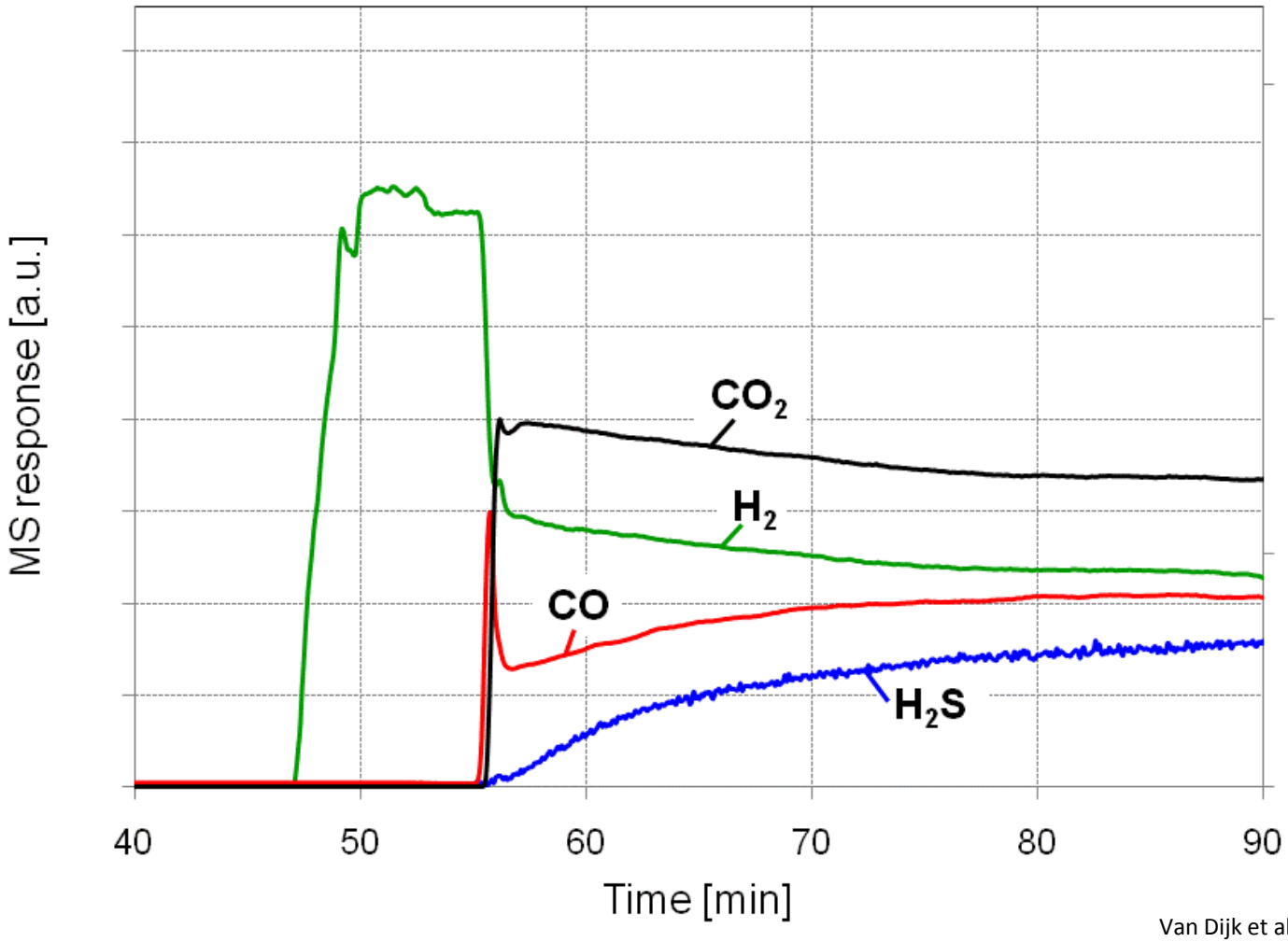



400 °C

1.5 bar

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

# 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

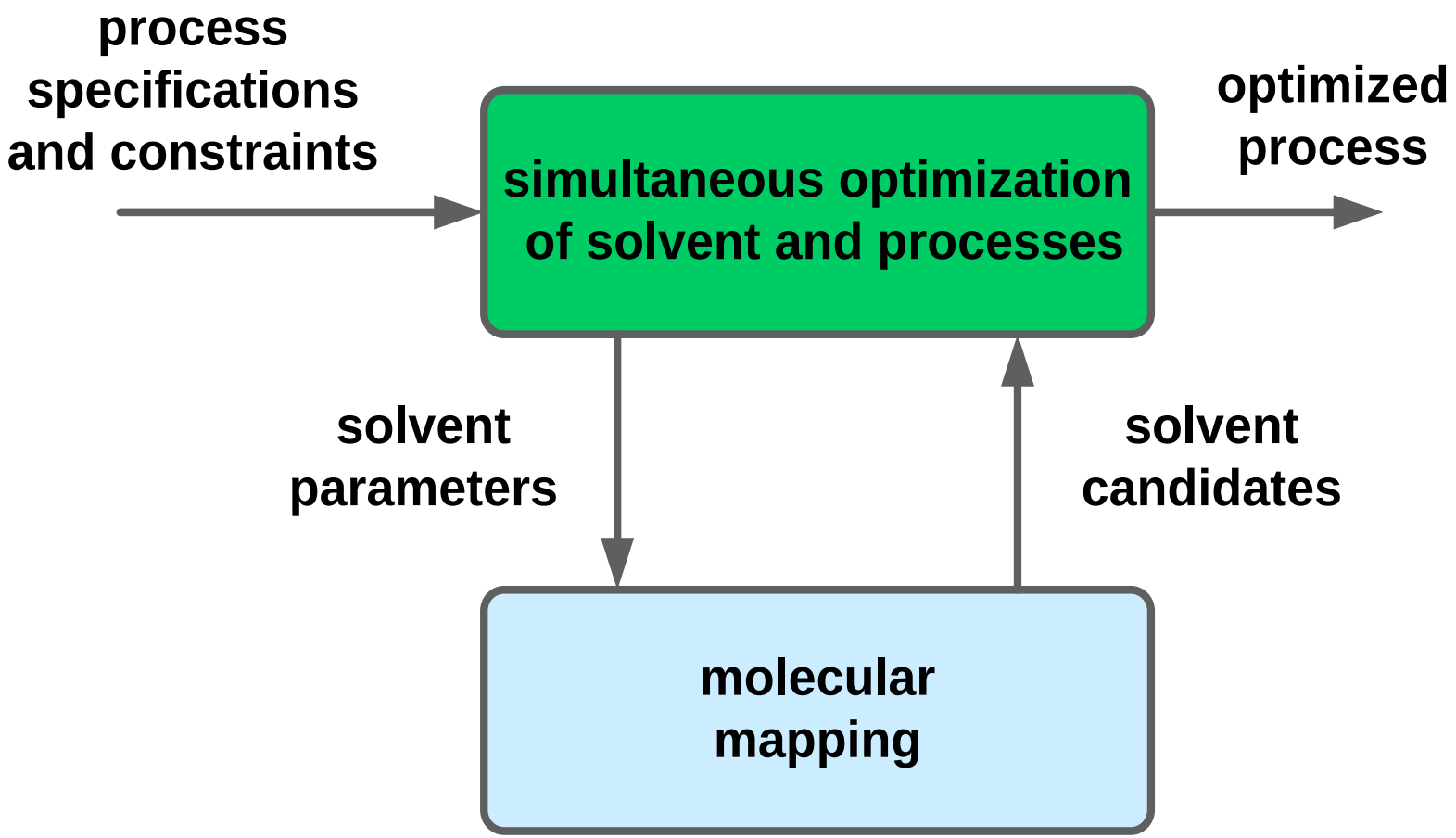
# Performance comparison

| 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 |

Gazzani et al. GHGT-10

# Catch-Up Pilot Plant, Buggenum

# Catch-Up Pilot Plant, Buggenum




Damen et al. GHGT-10

# 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
Hot gas clean-up
Process intensification (sorption-enhanced reactor)

# Acknowledgements

caesar.ecn.nl

CACHET CO2

CAP TECH

cato

Agentschap NL
Ministerie van Economische Zaken