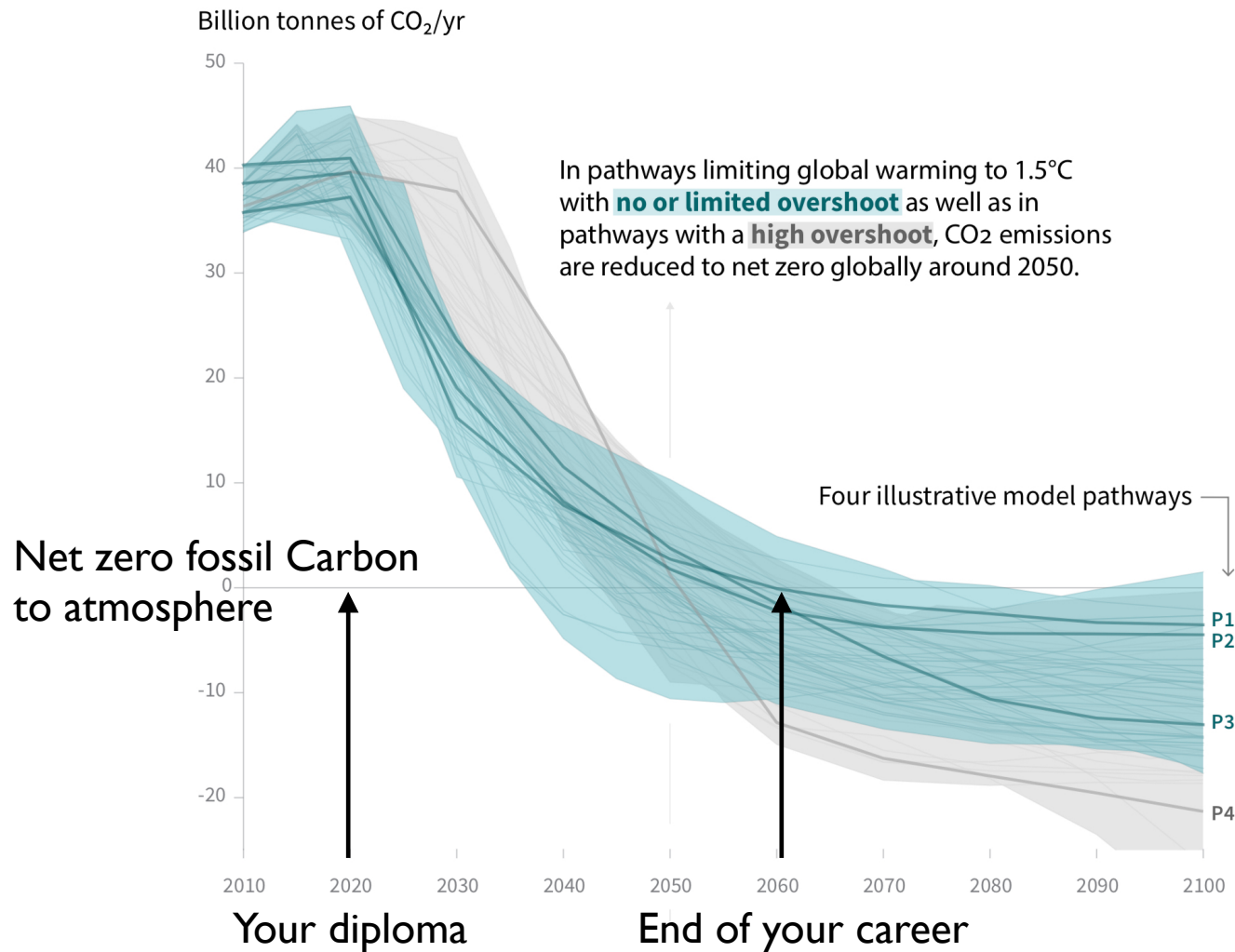


The Paris agreement challenge (COP 21)



20% : our remaining carbon budget

2.5% : world GDP to invest each year

1CHF/day/cap :
the contribution of Swiss citizens

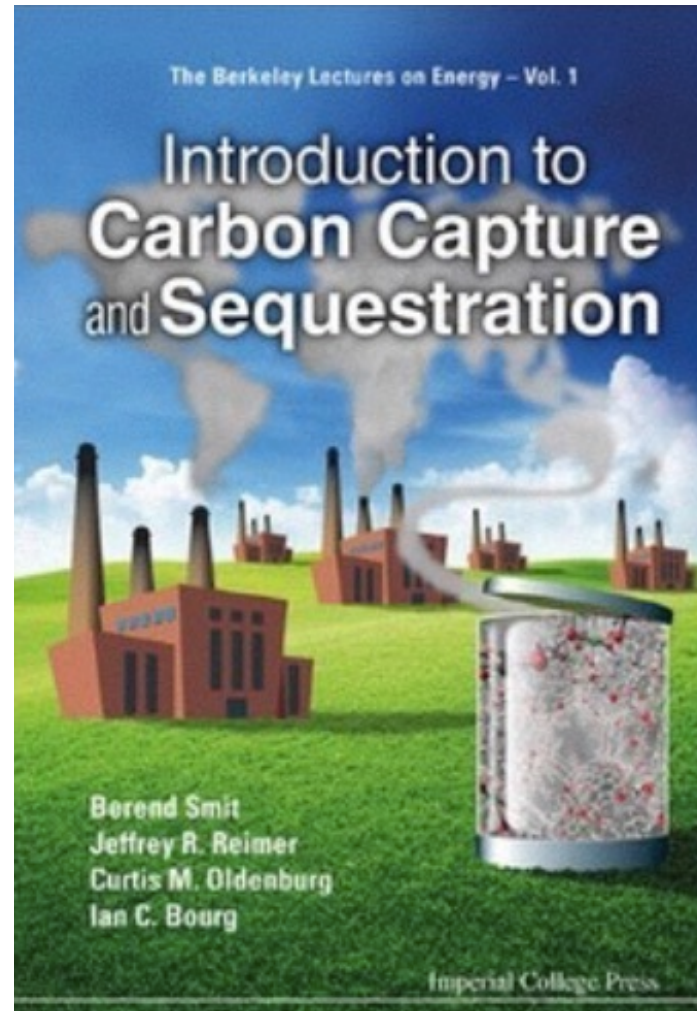
<http://ipcc.ch/report/sr15/>

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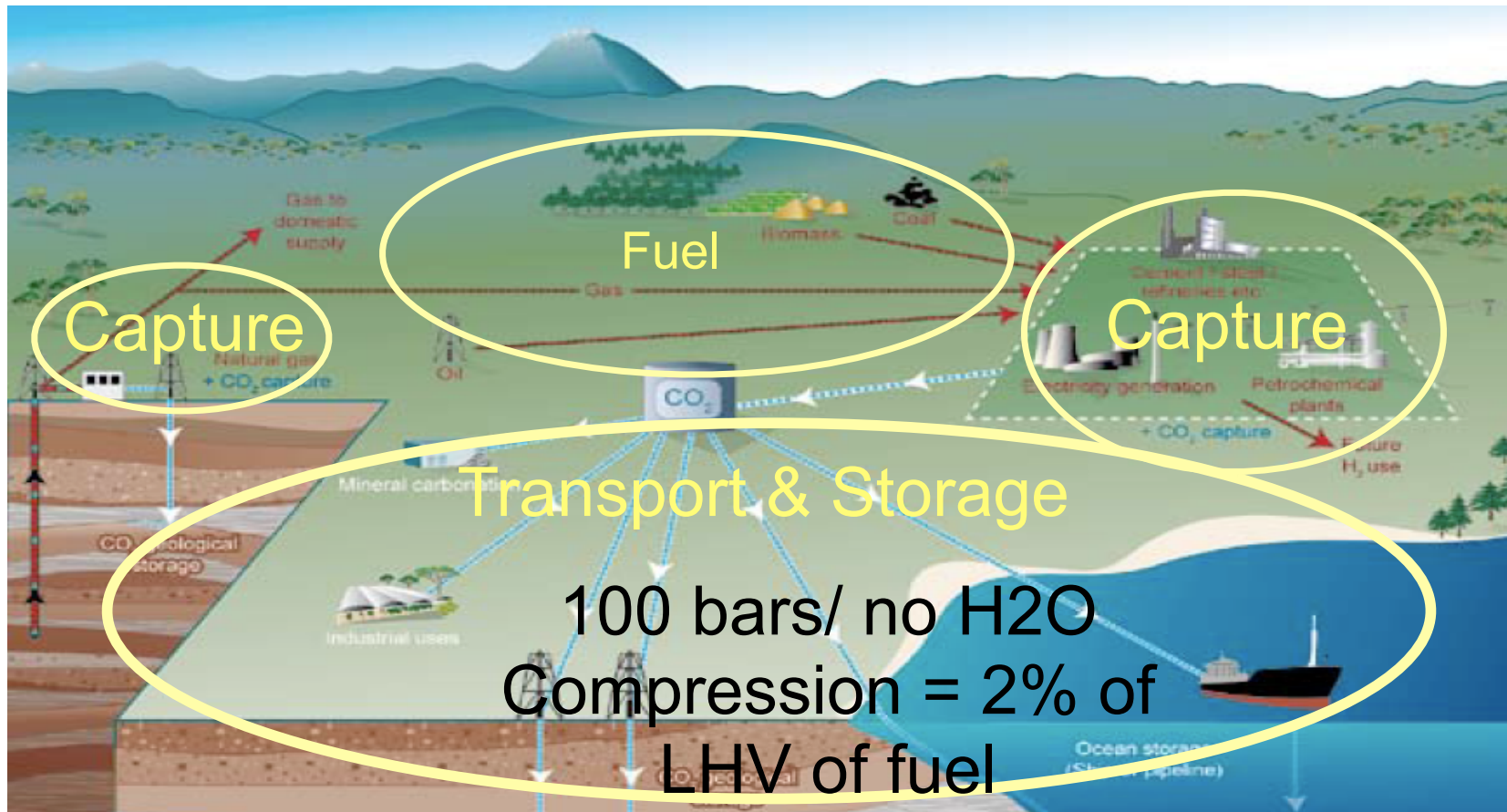
CO₂ Capture, Sequestration and Re-Use

Prof. François Marechal

Further readings

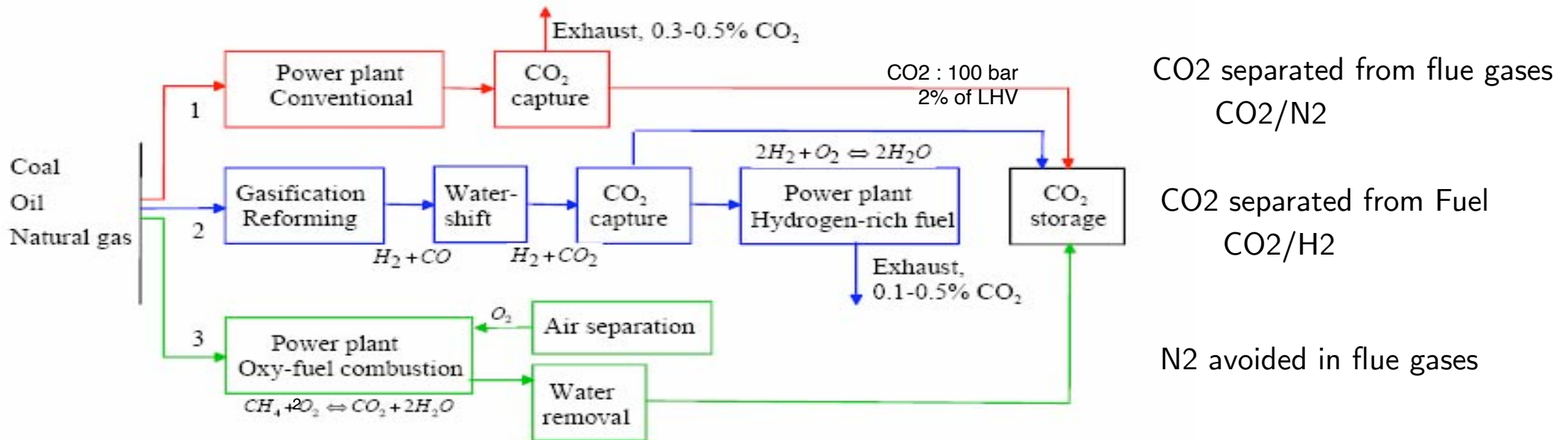
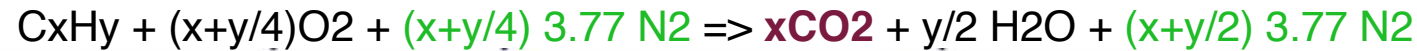


CO₂ capture and storage (CCS)



(source : IPCC CCS Report)

CO2 capture in power plants



1: Post-combustion principle

2: Pre-combustion principle

3: Oxy-fuel principle = direct stoichiometric combustion with oxygen

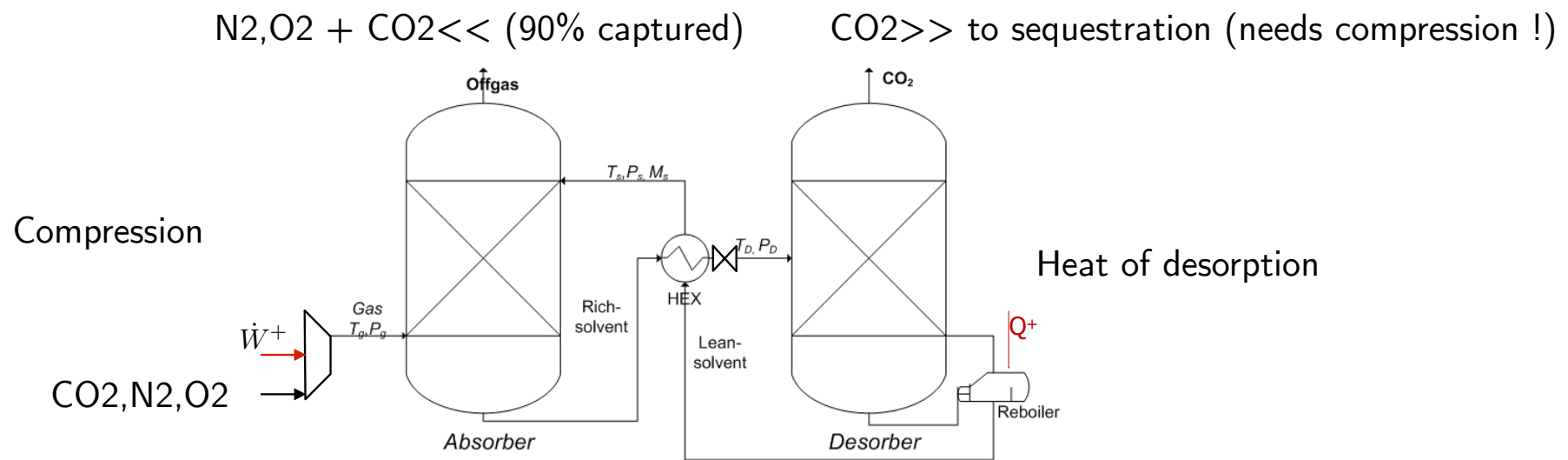
Fig. 3.17 Options for CO₂ separation [16]

Ab(d)sorption systems

- Temperature and pressure conditions
- CO₂ delivery conditions for transport and sequestration

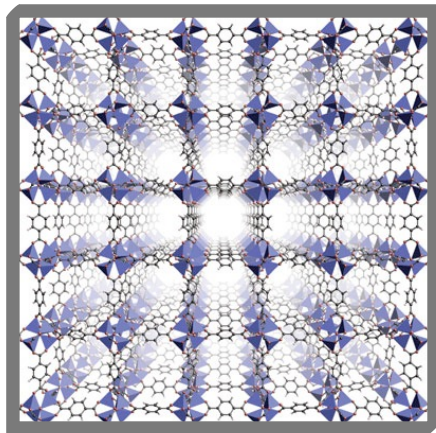
Table 1: Comparison of physical and chemical ab- and adsorption for CO₂ separation [13].

Process	Conditions	Gas removed	Thermal Energy kWh/kgCO ₂	Mechanical work kWh/kgCO ₂	CO ₂ purity %
Rectisol	$T_{abs} \approx -10 / -70^\circ C$ $p_{CO_2} > 10 \text{ bar}$	CO ₂ , NH ₃ H ₂ S, COS, HCN	0.025	0.038	< 90%
Selexol	$p_{CO_2} \approx 7-30 \text{ bar}$	CO ₂ , NH ₃ H ₂ S, COS, HCN	0.016-0.024	0.03-0.06	
MEA	$T_{abs} \approx 40^\circ C$, 1-5bar $T_{desorb} = 95 - 120^\circ C$	CO ₂ , CS ₂ H ₂ S, SO ₂ , COS	2.3	0.05-0.3	< 99%
PSA-Flue gas 28-34% CO ₂	$P_{ad} = 1 \text{ bar}$, $P_{desorb} = 0.05 - 0.9 \text{ bar}$	CO ₂	0.16-0.18		
PSA - syngas	$P_{ad} = 13 - 21 \text{ bar}$, $P_{desorb} < 1 \text{ bar}$	CO ₂			> 90%

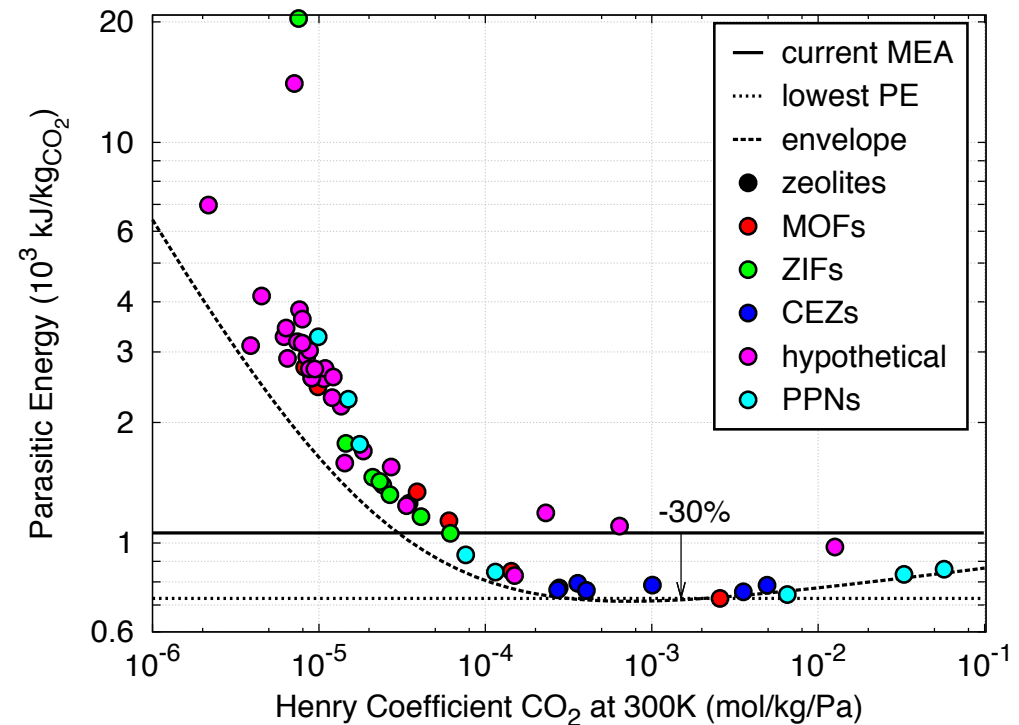


Research in new adsorbent

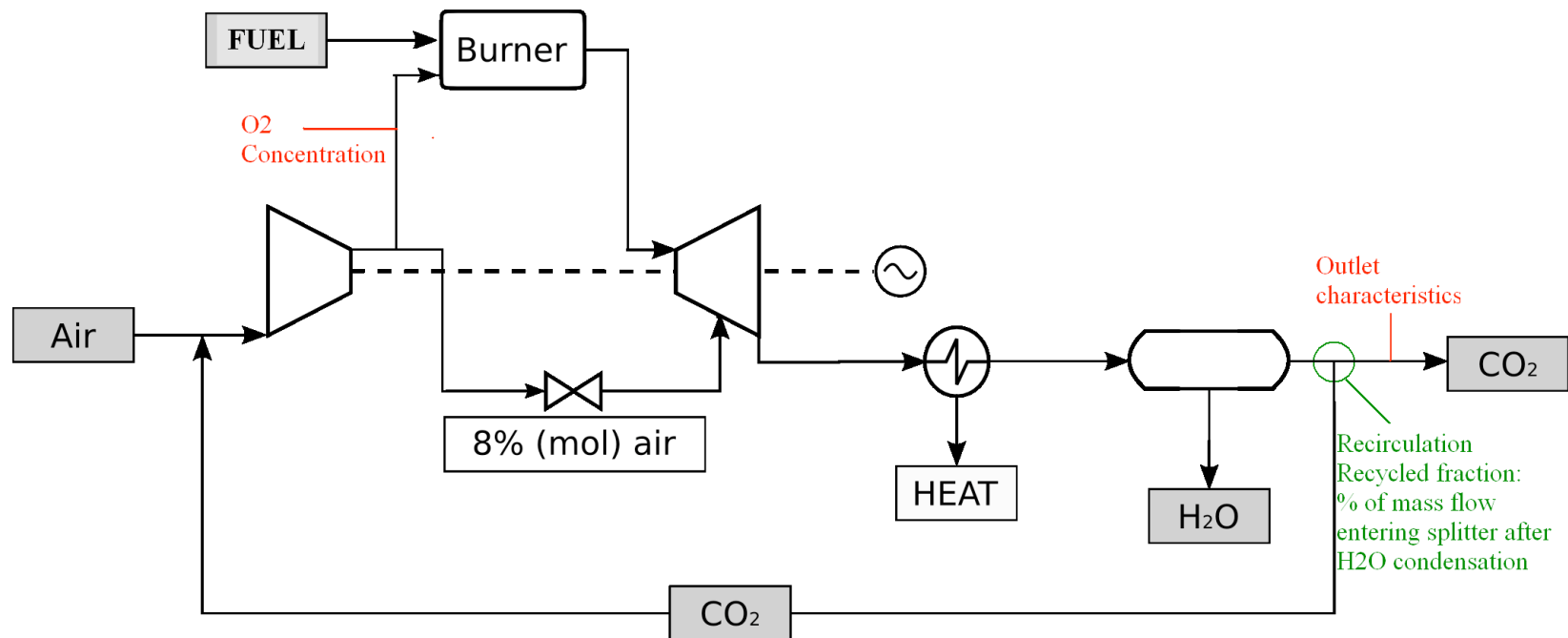
MOFs (Metal Organic Frameworks), Zeolites



$\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$
MOF-5



Increasing CO₂ concentration



CO₂ Recirculation allows for higher CO₂ partial pressure in the absorber => lower investment cost
O₂ excess lower in the burner => flame stability problems

Heat integration

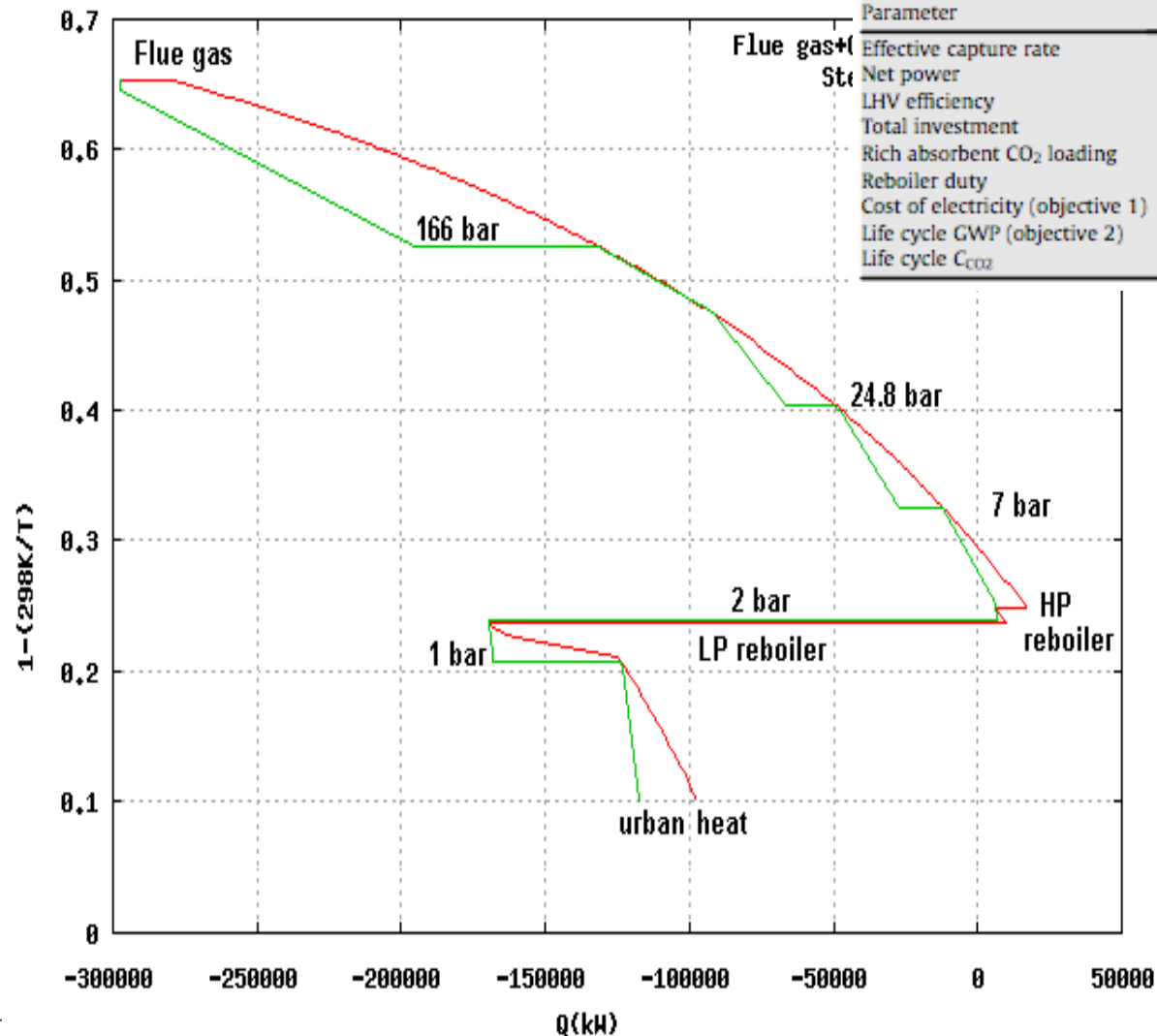


Table 4

Additional details on the b2 and b5 designs.

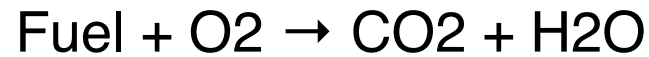
Parameter	Unit	Design b2	Design b5
Effective capture rate	%	90.2	96.4
Net power	MW	363	360
LHV efficiency	%	54.5	54.0
Total investment	M\$	351	357
Rich absorbent CO ₂ loading	mol CO ₂ /mol MEA	0.465	0.461
Reboiler duty	GJ/ton CO ₂ captured	3.45	3.46
Cost of electricity (objective 1)	\$/MW h	78.31	79.85
Life cycle GWP (objective 2)	kg CO _{2eq} /MW h	111.9	88.4
Life cycle C _{CO2}	\$/kg CO _{2eq}	62.43	62.67

Efficiency drop
from 59% to 54% !

Cost of electricity
+20 \$/MWhe
(+50%)

The heat of desorption reduces the
electricity produced
Heat of adsorption can be recovered

Oxyfuel route



No N₂ in the flue gases

CO₂ separation by condensing H₂O

O₂ to be produced from Air

- * needs a Air Separation Unit
- * consumes Elec

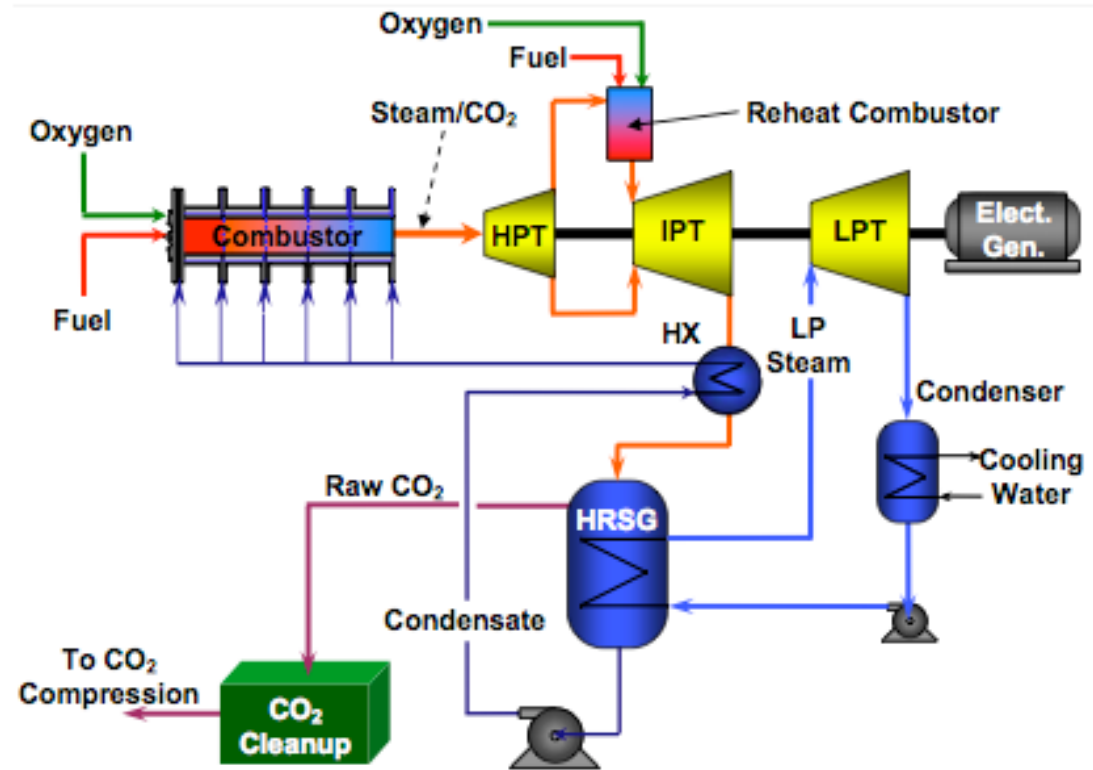


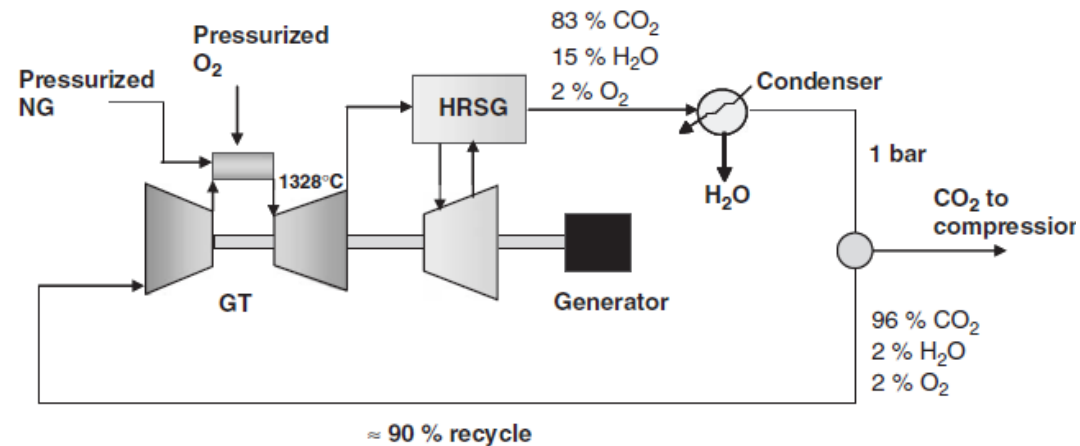
FIGURE 3. Conceptual Layout of CES Oxy-Fuel Cycle

Oxyfuel in gas turbine

- Oxy-fuel combustion
- Matiant O_2/CO_2 cycle

Exhaust gas used as working fluid

CO_2 recycled to combustor to keep turbine inlet temperature (TIT) at required level



*Kvamsdal et al.
Energy 32 (2007)*

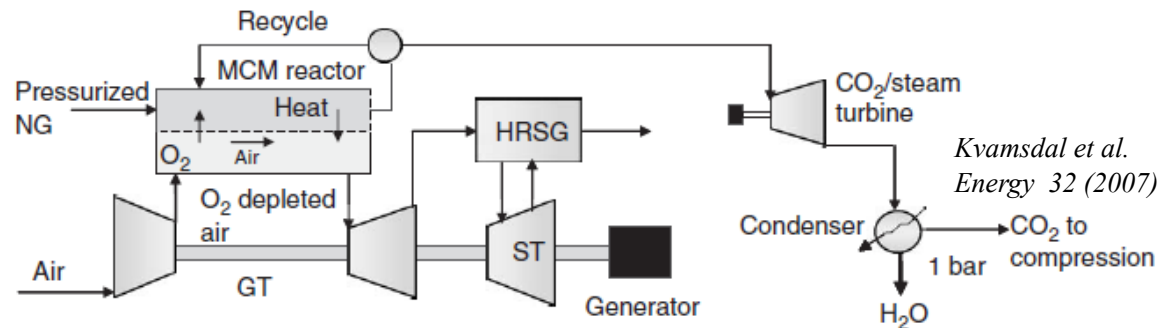
- ❑ Matiant cycle: increase of efficiency by increasing the upper cycle pressure and inserting a reheat
- ❑ Efficiency: max 45%

Oxyfuel route : separation with membranes

- Oxy-fuel combustion

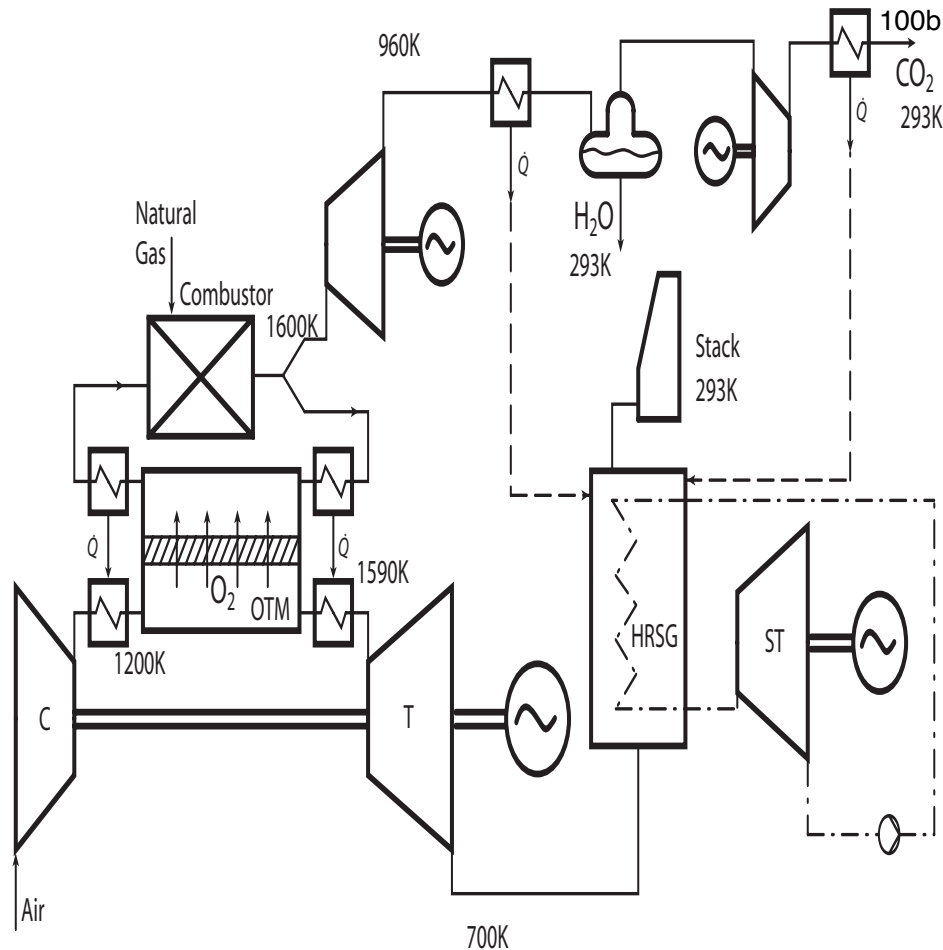
- AZEP (Advanced zero emission power plant) concept
- Combustor replaced by mixed conductive membrane reactor (MCM)

- Separation of O_2 from air by membrane
- Near-to-stoichiometric fuel combustion
- Heat exchange



- Efficiency: 55-62%
- Specific cost: 690-1404\$/kW

Oxy-fuel : AZEP Plant (Alstom)



	Solution A	Solution B
Gas Turb. press. ratio	18	41
OTM inlet temp.	1200 K	1200 K
Oxygen sep. ratio	21.8%	31.2%
OTM outlet HX ΔT	100 K	97 K
Combustor out. temp.	1600 K	1600 K
Steam head. press.	101 bar	102 bar
	14 bar	13 bar
	2 bar	1 bar
Steam head. superh.	357 K	365 K
	311 K	214 K
	283 K	290 K
Condensate head. press.	0.021 bar	0.020 bar
ΔT multiplication factor	1	1
Specific Cost	690 US\$/kW	1404 US\$/kW
Efficiency	55.1%	62.5%

OTM : Oxygen separation membrane
 Ceramic Separation membrane at high temperature (900 °C)

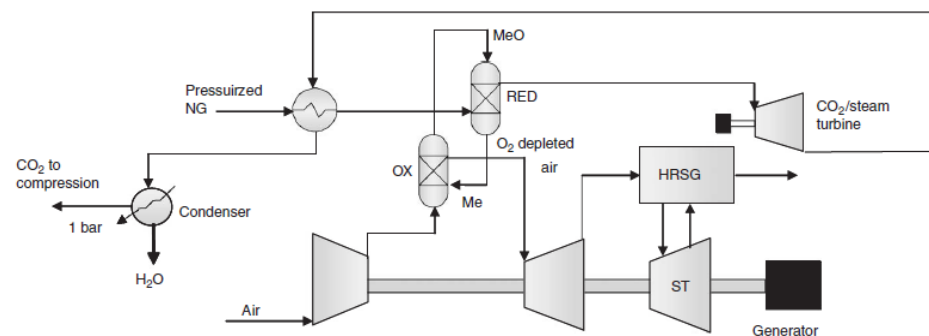
Chemical looping Combustion

CO₂ capture concepts

- Oxy-fuel combustion

- Chemical looping combustion (CLC)

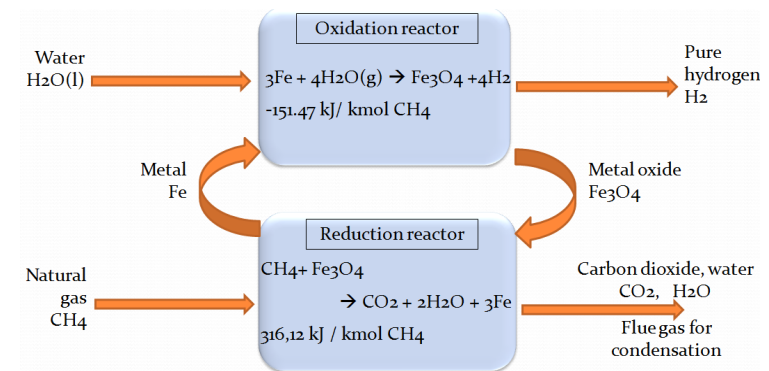
- No direct contact between air and fuel
- Combustion process split up into oxidation and reduction
- Metal oxide as oxygen carrier



*Kvamsdal et al.
Energy 32 (2007)*

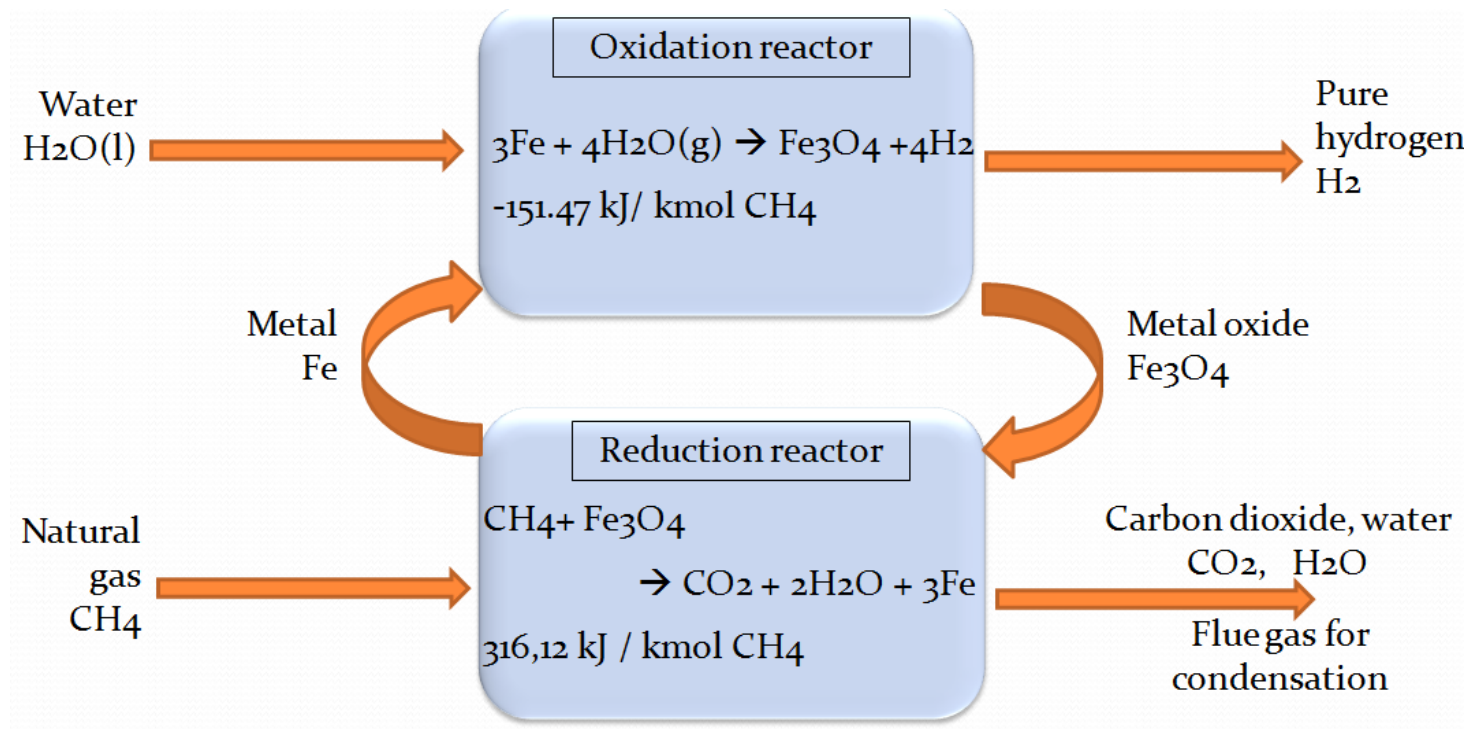
□ Efficiency: 51%

□ Alternative H₂ co-production



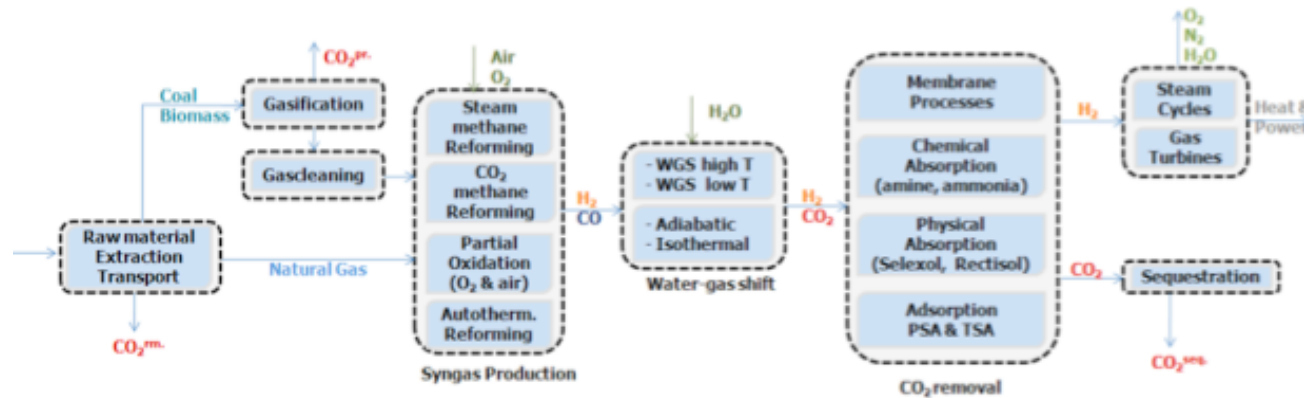
*Courjon
EPFL/LENI (2010)*

Chemical looping



*Courjon
EPFL/LENI (2010)*

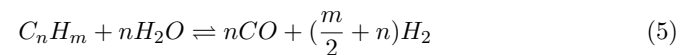
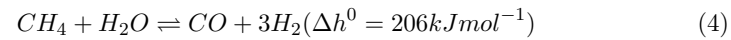
Hydrogen production routes



C_xH_y

Steam Methane reforming

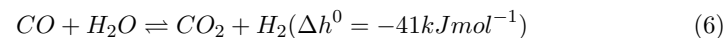
$CO + H_2$



This reaction is equilibrated and takes place simultaneously with the shift reaction, therefore the resulting gas mixture always contains the four components.

Water gas shift reaction

$CO_2 + H_2$



H₂/CO₂ separation

H_2

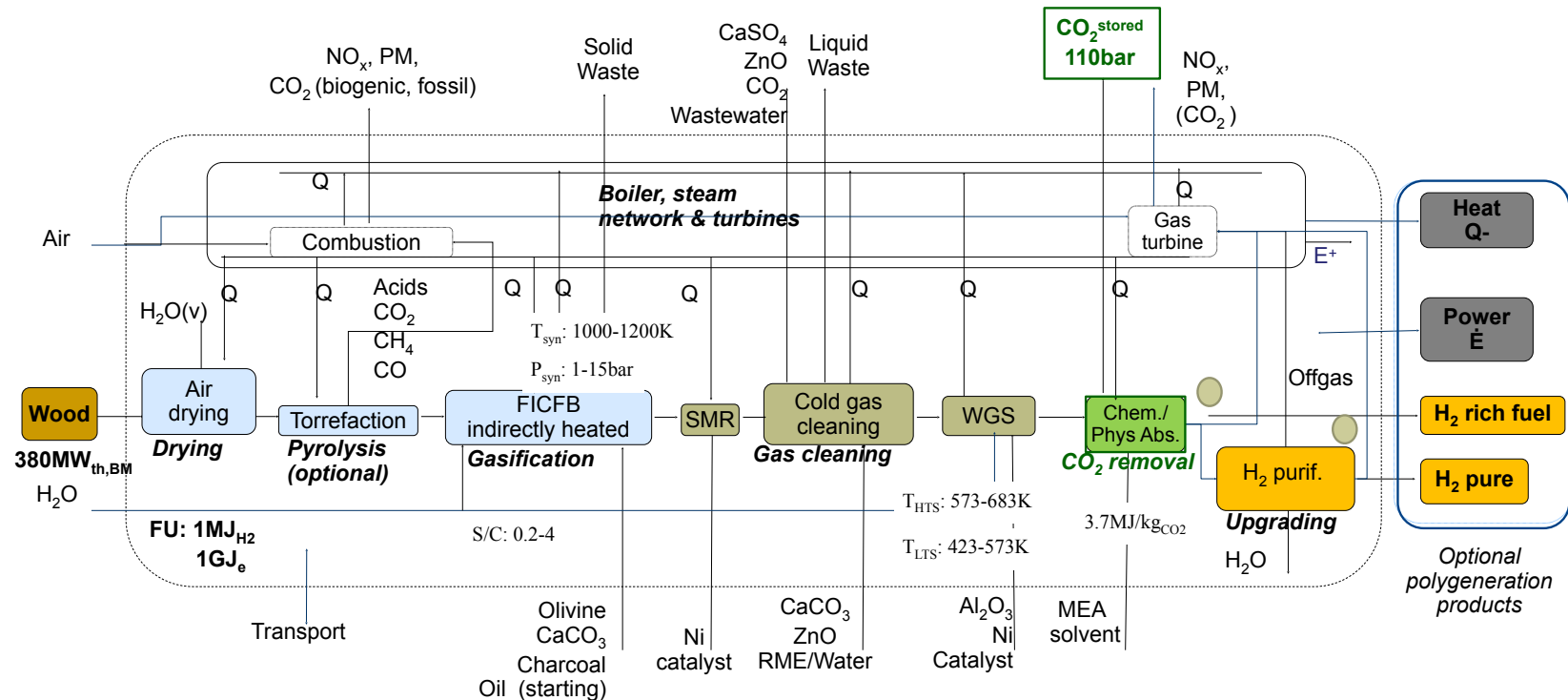
CO_2

CO_2 is separated from the H_2
 H_2 is then the fuel for a combined cycle or a fuel cell

Table 1. Reaction properties for a conventional steam methane reformer (SMR).

General info:	Endothermic reaction
Temperature	500 – 1000 °C
Pressure	1 – 30 bar
Steam/methane ratio	2 – 3,5
Catalysts	Nickel- and aluminium oxide-based catalysts

Electricity production using biomass with CO2 capture

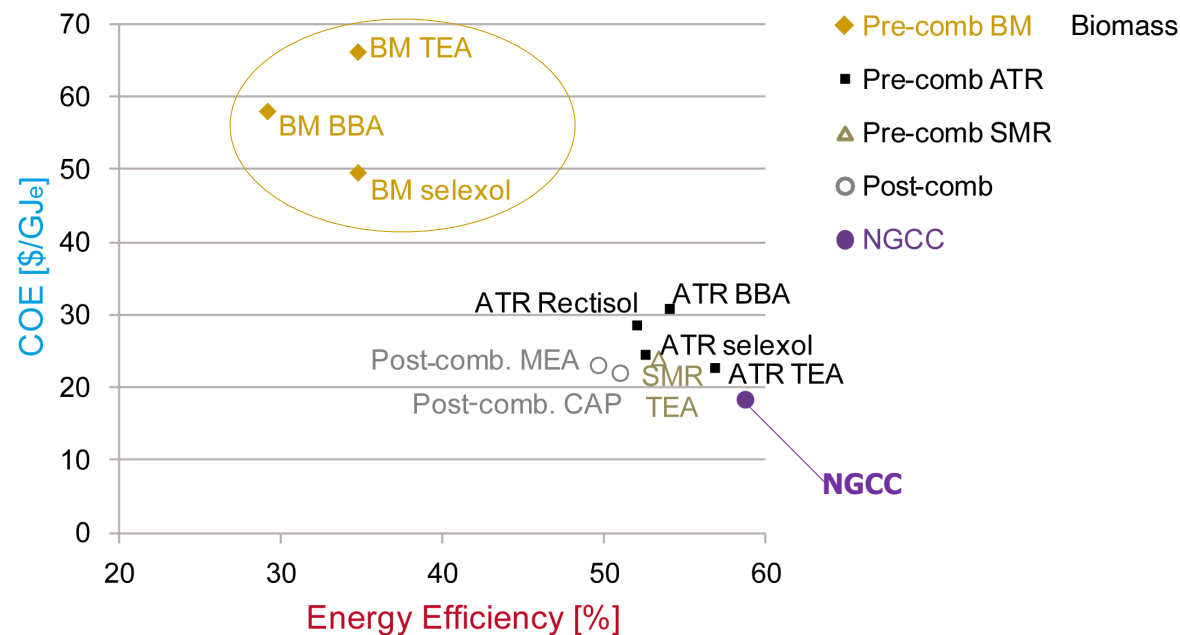


- Configurations (380MW_{th,BM})
 - Without/with CO₂ capture (compression to 110bar)
 - H₂ process with $\dot{E}$ import or self-sufficient or $\dot{E}$ generation

CO₂ capture options comparison

CO₂ capture energy and cost penalty

- Different process configurations
 - Natural gas fed processes 90% CO₂ capture, biomass 60% capture

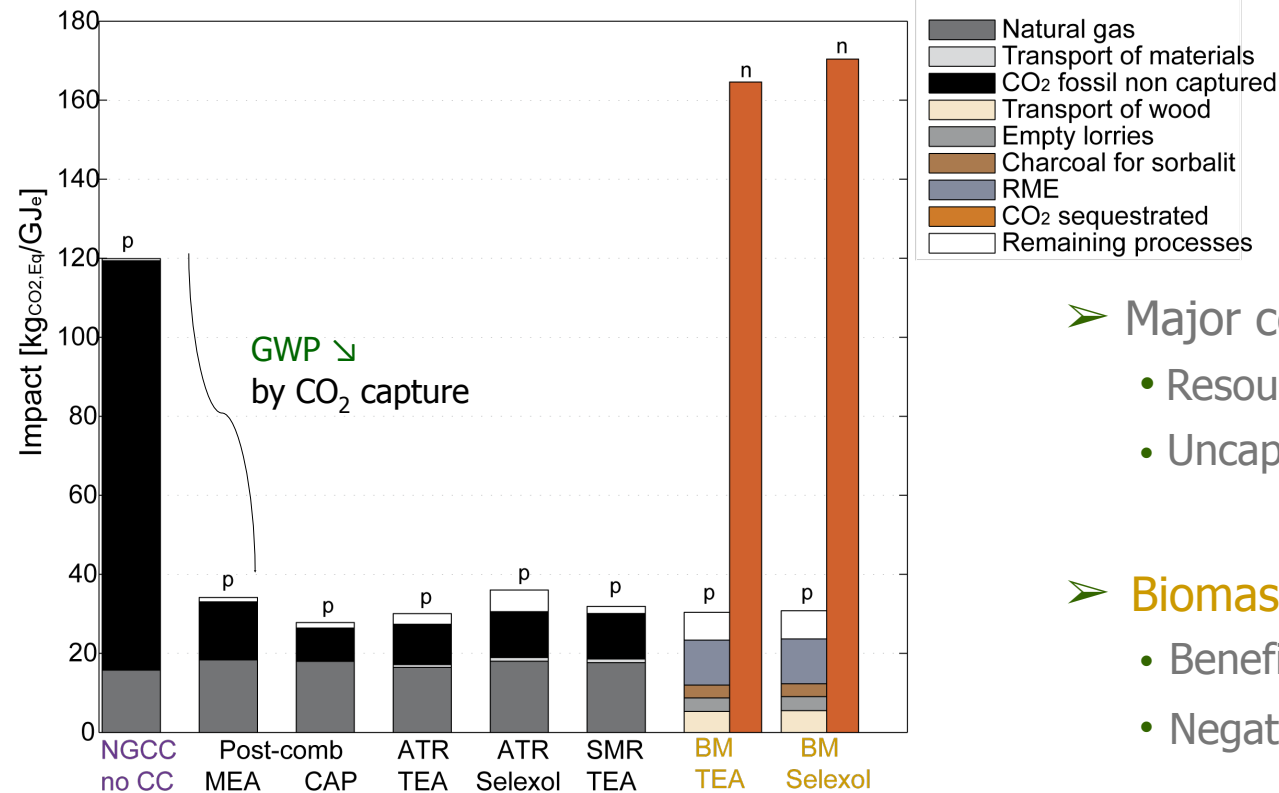


- Competition between post- and pre-combustion

CO₂ capture options comparison

CO₂ capture environmental performance

- IPCC 07: Global warming potential (FU=1GJe)



➤ Major contributions

- Resource extraction
- Uncaptured CO₂

➤ Biomass fed process

- Benefit of capturing biogenic CO₂ !
- Negative carbon balance !

Decision-making

Most economically competitive process configurations

System	NGCC	Post-comb	ATR	BM
Performance	no CC	MEA	Selexol	Selexol
Feed [MW_{th}]	559	582	725	380
CO ₂ capture [%]	0	82.9	78.6	69.9
ϵ_{tot} [%]	58.75	50.6	53.5	35.4
Net electricity [MW_e]	328	295	383	135
[$kg_{CO_2, local}/GJ_e$]	105	13.9	22.2	-198.1
COE incl. tax [$\$/GJ_e$]	18.2-28.8	9-40	12.8-42	15-69
Avoid. Costs incl. tax [$\$/t_{CO_2, avoided}$]	-	-63-121	-49-127	0-253

➤ CO₂ capture penalty

- **Efficiency** ⬇: 6-10%-pts
(CO₂ compression ~2%-pts)
- **COE** ⬆: 20-25%

➤ Best performing process

- **Efficiency**: Nat gas. pre-comb.
- **Economic**: Nat gas. post-comb.
- **Environmental**: Biomass pre-comb.

➤ Competition between processes and objectives!

CO2 mitigation cost

Table 7

Performance of the different power plant options with CO₂ capture.

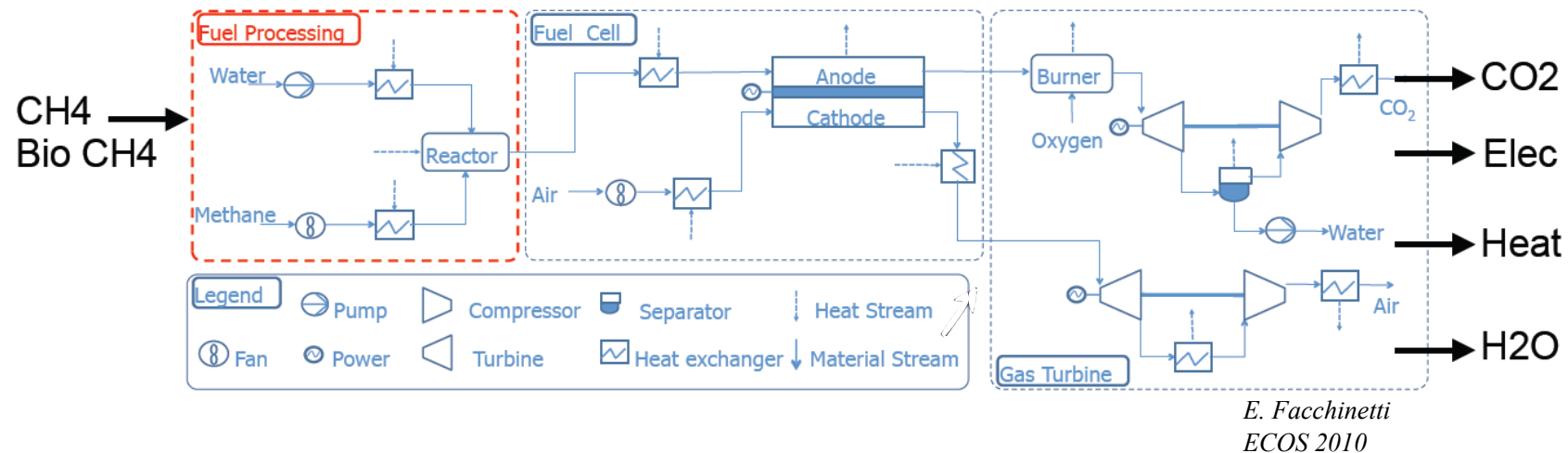
System capture technology	NGCC no CC	Post-comb MEA	Post-comb CAP	ATR TEA	ATR Selexol	SMR TEA	BM TEA	BM Selexol
Feed [MW _{th,NG/BM}]	559	587	588	725	725	725	380	380
CO ₂ capture [%]	0	89.5	89.7	89.7	89.1	89.3	59	59
€ _{tot} [%]	58.75	49.6	50.9	56.8	52.6	53.3	34.8	34.8
Power balance								
Net electricity [MW _e]	328	291	299	408	375	381	132	132
$\dot{E}_{consumption}^{+}$ [MJ _e /GJ _{e,net}]	–	108.3	44	91.9	146.6	48.1	342.4	342.4
$\dot{E}_{steamnetwork}^{-}$ [MJ _e /GJ _{e,net}]	340.7	341.3	301	200	177.6	143.8	346.2	346.2
$\dot{E}_{gasturbine}^{-}$ [MJ _e /GJ _{e,net}]	659.3	767	743	891.9	969	904.3	996.2	996.2
Economic performance (assumptions Table 10 – base)								
Invest. [\$/kW _e]	555	909	785	757	813	798.8	7380	3880
COE no CO ₂ tax [\$/GJ _e]	18.31	23.7	22.5	22.67	24.5	24.1	66.1	49.5
COE with CO ₂ tax [\$/GJ _e]	22	24.2	22.8	23.0	24.9	24.5	60.2	43.6
Avoidance costs [\$/t _{CO₂,avoided}]	–	60	43	46	66	62	173	113
Environmental performance (FU = 1GJ _e)								
CO ₂ emissions [kg _{CO₂} /GJ _e]	105	14.9	8.5	10.1	11.5	11.2	–170.4	–170.4
IPCC GWP [kg _{CO₂,eq} /GJ _e]	120	34	27.7	30	31.9	36.1	–139.6	–134.2
EI99 [pts/GJ _e]	7.48	7.7	7.7	7.7	8.1	9.0	6.2	6.1
Impact 2002 [10 ^{–3} pts/GJ _e]	28.9	20.8	20.3	21.5	22.4	25	2.9	3.2
CML acidification [10 ^{–2} kg _{SO₂,eq} /GJ _e]	20.1	14.9	15.4	20.6	21.8	24.3	21.3	21.1
CML eutrophication [10 ^{–3} kg _{PO₄,eq} /GJ _e]	39	23.6	24.4	37.7	40.6	43.5	95.1	95

Scenario	Base
Resource price [\$/GJ _{res}]	9.7
Carbon tax[\$/t _{CO₂}]	35
Yearly operation [h/year]	7500
Expected lifetime [years]	25
Interest rate [%]	6
Biomass feed [MW _(th)]	380
NG feed (post-comb) [MW _(th)]	725
NG feed (pre-comb) [MW _(th)]	590

Tock, Laurence, and François Maréchal. "Thermo-environmental optimisation strategy for fuel decarbonisation process design and analysis." *Computers & Chemical Engineering* 83 (2015): 110-120.

CO₂ capture

- Fuel cell gas turbine hybrid system
 - SOFC => O₂ separation membrane
 - Innovative cycle with CO₂ capture
 - Energy efficiency 83%
 - Exergy efficiency >75%



Facchinetti, Emanuele, Daniel Favrat, and François Marechal. "Innovative Hybrid Cycle Solid Oxide Fuel Cell-Inverted Gas Turbine with CO₂ Separation." *Fuel Cells* 11.4 (2011): 565-572.

CO₂ capture: Performance

◆ Fuel decarbonization performance

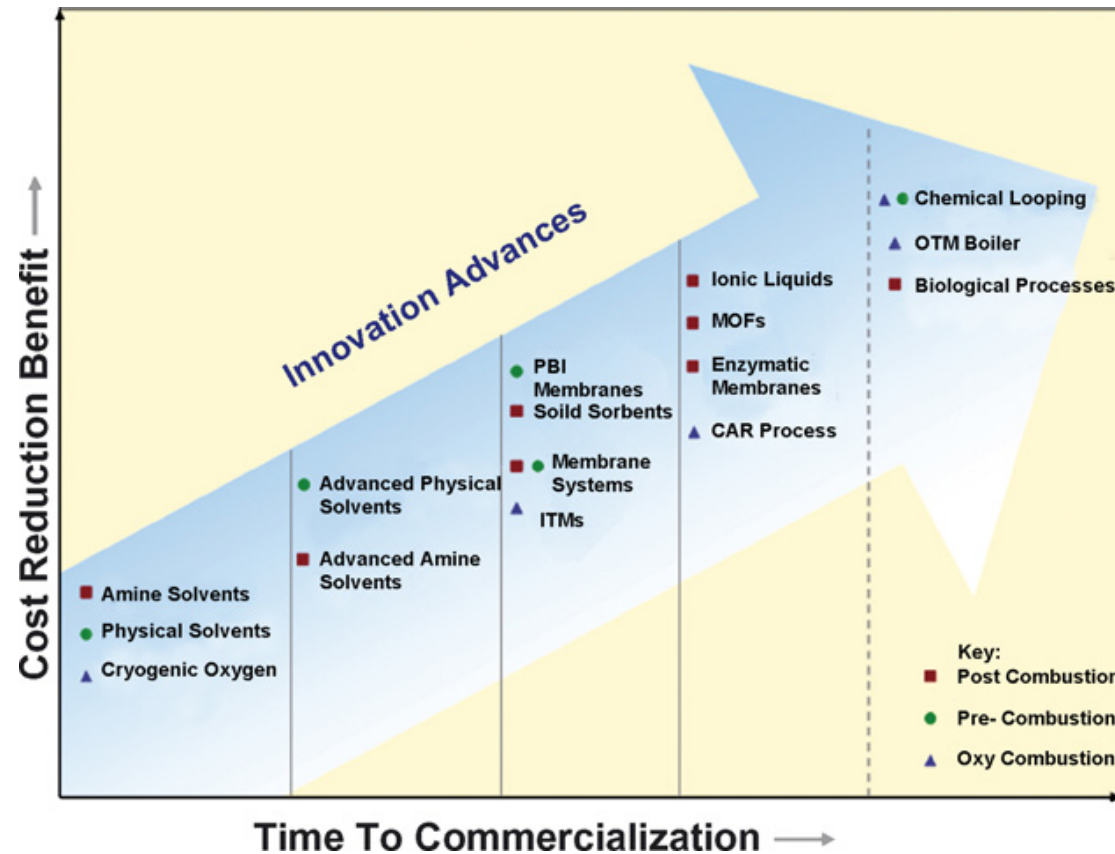
Electricity	PC			IGCC		NGCC				H₂ plant	
Capture	no	Post	Oxy	no	Pre	no	Post	Oxy	Pre	no	Pre
η [%] ¹	45	30	35	41-44	33	60	50	48	46		52-68
CO ₂ emissions [kg/MWh] ²	833	58	-	688	105	343	43	-	42	493	61
COE [\$/MWh] ⁴	43-52	62-86	61-80	41-61	54-79	31-50	← 43 – 72 →			23-36	27-48
\$/to CO ₂ captured ⁴	-	29-51	-	-	13-37	-	← 37-74 →				2-56

➤ With CO₂ capture: Efficiency ↘, COE ↗

- Without capture 400-800MW_e, with capture 300-700MW_e
- Up to 10% points lower efficiency
- Additional COE 10-30\$/MWh, ~50% higher COE

1. Kanniche M. et al., Pre-combustion, post-combustion and oxy-combustion in thermal power plant for CO₂ capture, *Appl. Therm. Eng.* 30, no.1, 53-62, 2010.
2. Parsons E.L. et al., Advanced fossil power systems comparison study: Final Report, *NETL*, 2002.
3. Klett. et al. Hydrogen Production Facilities Plant Performance and Cost Comparisons. United States Department of Energy – *NETL*, March 2002
4. Metz, B et al., IPCC Special Report on Carbon Dioxide Capture and Storage, *Cambridge University Press*, 2005

Carbon capture technology



[1] Figueroa, J. D.; Fout, T.; Plasynski, S.; McIlvried, H. & Srivastava, R. D. Advances in CO₂ capture technology – The U.S. Department of Energy's Carbon Sequestration Program. *International Journal of Greenhouse Gas Control*, **2008**, 2, 9 - 20