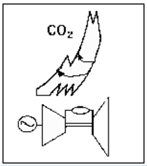

ZERO EMISSION TECHNOLOGIES : AN OPTION FOR CLIMATE CHANGE MITIGATION

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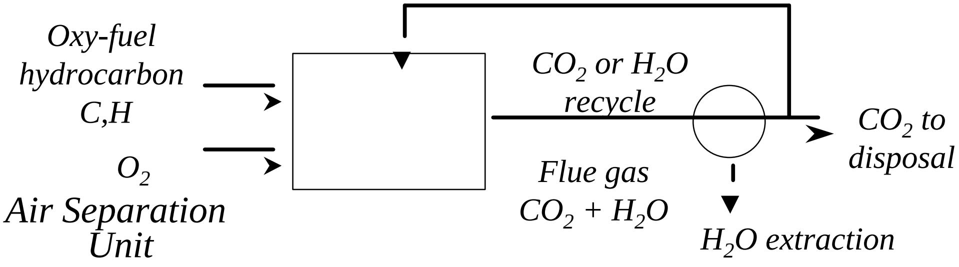
Basic principle of a Zero-Emission Power Cycle (O_2/CO_2 or O_2 /H_2O cycles)



Oxy-fuel hydrocarbon C,H

O_2

Air Separation Unit

CO_2 or H_2O recycle

Flue gas $CO_2 + H_2O$

CO_2 to disposal

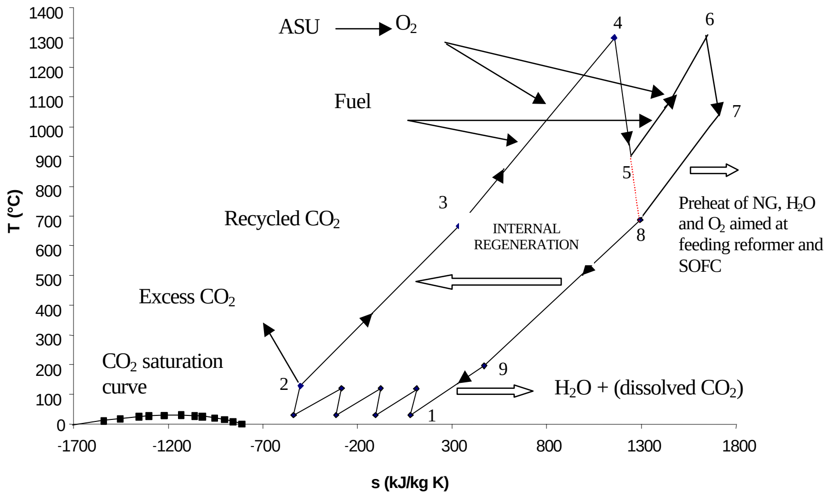
H_2O extraction

- O_2/H_2O and O_2/CO_2 : near Zero Emission Power Cycles use of O_2 as the fuel oxydiser produced in an air separation unit (ASU) and of H_2O or CO_2 as the cycle working fluid and thermal ballast for flame temperature control

Rationale of oxy-fuel cycles for Near Zero Emission Power Generation

- Use of nearly pure O_2 (+ Ar) as fuel oxidiser so that the flue gas is highly enriched in CO_2 : air separation required
- Use of CO_2 itself or of H_2O as the working fluid in a gas cycle and as thermal ballast for flame t° control in stoichiometric proportions
- Separation of CO_2 and H_2O is easy and there is no longer need for a very penalising scrubber separating CO_2 from N_2 in the flue gas
- Take advantage of the performance of most advanced GTs
- Two main options
  - ➢O_2/ H_2O cycles
  - ➢O_2/ CO_2 cycles
- CES water cycle; Graz cycle; AZEP cycle (Alstom/NorskHydro); HiOx (Aker Kvaerner); MATIANT

The regenerative E-MATIANT gas cycle



1-2 : intercooled staged compressor ; 2-3 : upper pressure cycle ; 3-4 : HP combustion chamber ; 4-5 : HP expander ; 5-6 : LP combustion chamber ; 6-7 : LP expander ; 9-1 : water cooler/separator ; 4-5-8 : non reheated expansion.

Configurations of O_2/CO_2 *MATIANT* cycles

E-MATIANT cycle

Ericsson-like CO_2 regenerative gas cycle

Boundary conditions : TIT = 1300 °C; LP turbine exhaust gas : 700 – 750 °C complying with temperature limits of advanced materials in regenerator and HRSG

ASU, extracted CO_2, fuel and oxygen compressors in the system

Cooling of hot components with extracted CO_2 or with compressed N_2 from ASU

Pinch point at regenerator inlet : 100°C

Upper cycle pressure : > = 110 bar

Reheat pressure : optimised 25- 40 bar

Net cycle efficiency : 40- 45%

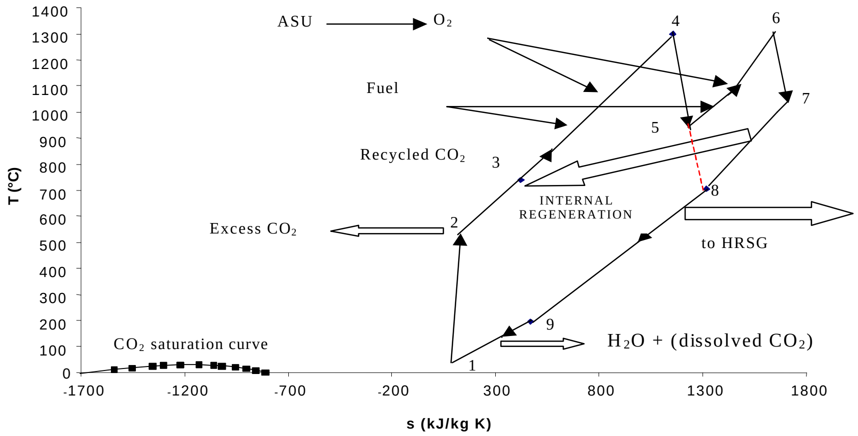
Improvements of O_2/CO_2 *E-MATIANT* cycles

- Recycling of the extracted water, superheated in the regenerator,in the LP combustion chamber: increase of specific power output and efficiency (similarly to STIG GTs)
- Use as a CC: adiabatic compressor and HRSG with advanced steam turbines (3PR, supercritical steam, 700°C) : **?** > 50%
- Use as an IGCC : addition of a gasification unit and a syngas clean-up unit downwards of the GT combustion chambers. Asset: the ASU is already existing; no need for a shift reaction of CO in the syngas and separation of CO_2 and H_2 : **?**~42- 45%
- Integration of a high t° fuel cells SOFC by the use of the sensible heat in hot exhaust flue gas (900°C) for preheating of fuel, O_2 and water/steam : **?** 47-49%
- Integration of a high t° conducting membranes (ITM or OTM) for oxygen production (900°C) : **?** ~45%

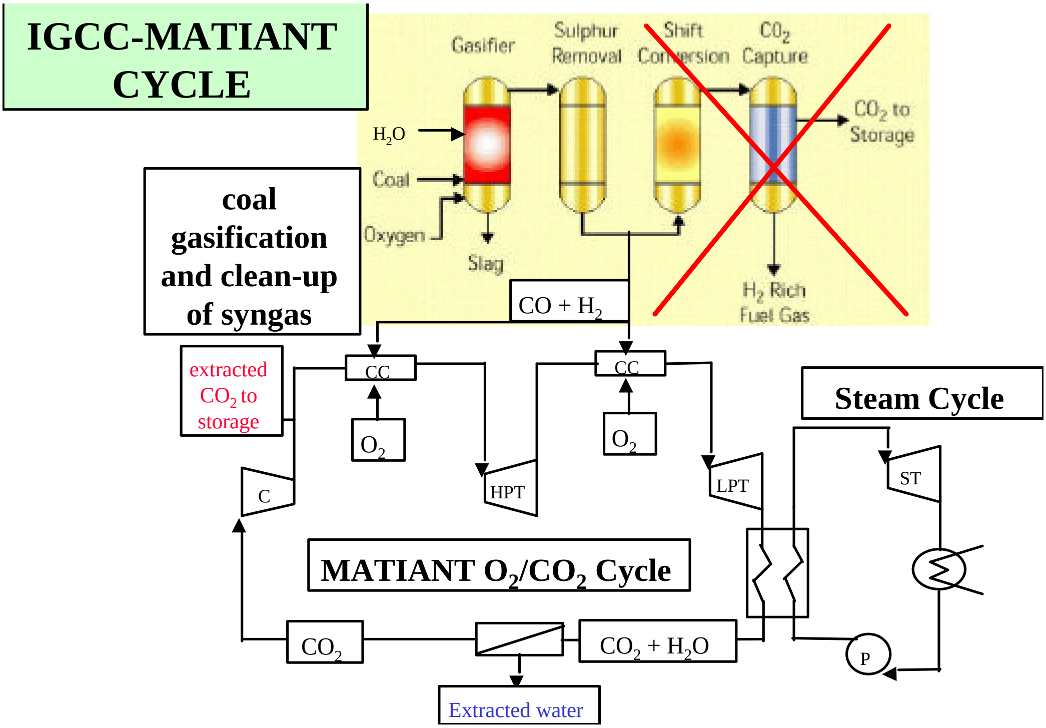
Modelling of the cycles : CO_2 properties

- Heavier than air and water (molecular weight: 44 against 29 and 18)
- Lower specific heat Cp than water (nearly the half) but roughly the same as air (for sizing of heat exchangers). Lower than air in the compression zone
- Lower adiabatic exponent γ = Cp/Cv (for sizing of turbomachines): less compressible than air and steam
- Low critical point (73 bar; 31°C) against 221 bar; 375°C for; water
- Higher density than water and lower in gaseous state than steam (influence on the dimensions of components)
- Chemically reactive (interaction with storage medium)
- **Supercritical CO_2 behaves like a liquid (density) and like a gas (viscosity)**

Combined Cycle based on a O_2/CO_2 Brayton–like gas cycle : CC-MATIANT cycle



Combined Cycle : O_2/CO_2 regenerative Brayton – like gas cycle with reheat and steam cycle with HRSG.
1-2 : adiabatic compressor ; 2-3 : upper pressure cycle ; 3-4 : HP combustion chamber ; 4-5 : HP expander ;
5-6 : LP combustion chamber ; 6-7 : LP expander ; 9-1 : water cooler/separator ; 4-5-8 : non reheated expansion.



COST OF CAPTURE or MITIGATION COST

- ⇨Definition : ratio of increase of the electricity cost ΔCOE (c€/kWh) and of CO_2 emission reduction ΔE (gCO_2/kWh)
- ⇨MC (Mitigation Cost) = ΔCOE/ ΔE (€/ton CO_2 avoided)
- ⇨COE_{st} = [I (capital cost/y) + O&M/y + F_{st} (fuel cost/y)]/PE (production/year)

  F_{st} = (€/kWh) = fuel cost (€/GJ)/ $?_{st}$ (kWh/GJ)
- ⇨COE_{ZEP}= [I(ZEP unit) + $O\&M_{ZEP}$]x[W_{st}/W_{ZEP}]+ F_{ZEP}/PE with F_{ZEP} (€/kWh) = fuel cost (€/GJ)/$?_{ZEP}$ kWh/GJ)= F_{st}x[W_{st}/W_{ZEP}]= F_{st}x[$?_{st}/?_{ZEP}$]
- ⇨$E_{ZEP} = E_{st} \times (1 – R) \times W_{st}/W_{ZEP}$ (R = 98%)

  $\Delta E = E_{st} - E_{ZEP} = E_{st}[1 - (1 – R) \times W_{st}/W_{ZEP}]$

  Reference NGCC $?_{st}$ = *55%;* E_{st} = *350* gCO_2/kWh

MITIGATION COST

COE for a E-MATIANT plant 5 –7 cent€/kWh

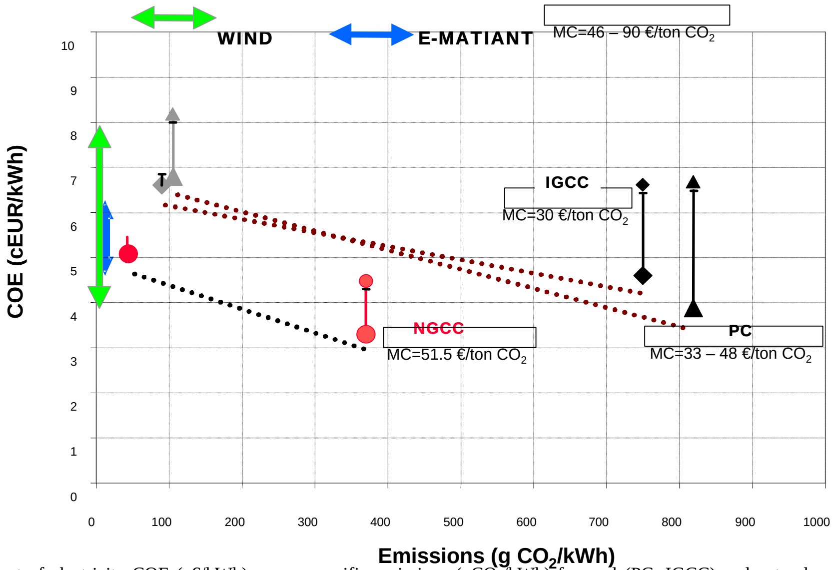
+ 50-100% above the COE of a standard NGCC

Comparable to COE of wind energy (‘4-8 cent€/kWh)

⇨ **MC : ranking of technologies with capture**

IGCC (30 €/ton CO_2 avoided) < PC (40.5+-7.5) < NGCC(50.5)

⇨ **MC for the E-MATIANT cycle is 45 – 90 €/ton CO_2 avoided and is in the same range of that of natural gas and coal fired plants with capture by chemical absorption in the flue gas (40 – 60 €/ton CO_2 avoided)**



Cost of electricity COE (c€/kWh) versus specific emissions (gCO_2/kWh) for coal (PC, IGCC) and natural gas (NGCC, E-MATIANT) power plants without and with capture and without and with the external costs (vertical bars). The mitigation costs (the slope of the straight lines) are mentioned for each technology.

Technical issues in ZEP cycles

- The technical issues are linked to the composition of the working fluid:design of turbomachines operating on CO_2 / H_2O; development of materials and cooling techniques
- Cooling systems of CO_2 expanders and combustors at 1300°C and higher
- Combustion in pure O_2 in a CO_2 atmosphere under pressure,in stoichiometric conditions → the flame stability is demonstrated at 1 bar
- Chemical behaviour of CO_2
- Oxygen production using high temperature membranes; chemical looping
- Development of high temperature steam turbines (>=700°C) cooled with steam : steam cooled GT

Advantages of ZEP cycles

- Low emission of CO_2 AND of NO_x, SO_2 and particulates (lower than in flue gas and fuel decarbonisation)
- Separation of CO_2 and H_2O is easy in a cooler separator or a condenser
- Modular structure and low degree of complexity (availability and reliability)
- High fuel flexibility : fossil fuels, biomass and hydrogen
- Performance improvements by the use of advanced GTs and boilers
- Possible integration of high t° fuel cells and ITM at high t°

Advantages of ZEP cycles

- No use of chemicals for capture (no emission of solvents)
- No waste products (possibly toxic) to dispose of
- High purity of the delivered dry CO_2 (water separation); the extracted CO_2 is contaminated with non condensible gases (Ar, NOx,N2 coming from ASU and fuel) and with impurities from the fuel like sulfur, metals
- Potential for use at small and large scale in off- and on shore applications
- Cost constrain on the GT : purchase price has to be 200 €/kW as for a current advanced industrial air based GTs

Conclusions

- ZEP cycles are only designed for CO_2 emission mitigation but at the same time they do not release other pollutants. Then the question about CO_2 purity for the sequestration arises
- They accept a large range of fuels like solid and liquid fuels, NG, syngas CO + H_2, hydrogen, biofuels, wastes…for combustion or gasification
- The various types of ZEP cycles (O_2 /H_2O and O_2 /CO_2 MATIANT cycles) have high and similar performance (40-5O% efficiencies) and very low specific emissions (a few gCO_2/kWh)
- Technical issues are solvable and ZEP cycles are feasible
- ZEP technology could be cost effective in a near future, especially in the framework of any kind of regulations on emissions and of fiscal measures (taxes, trading , certificates.)

FUTURE OBJECTIVES

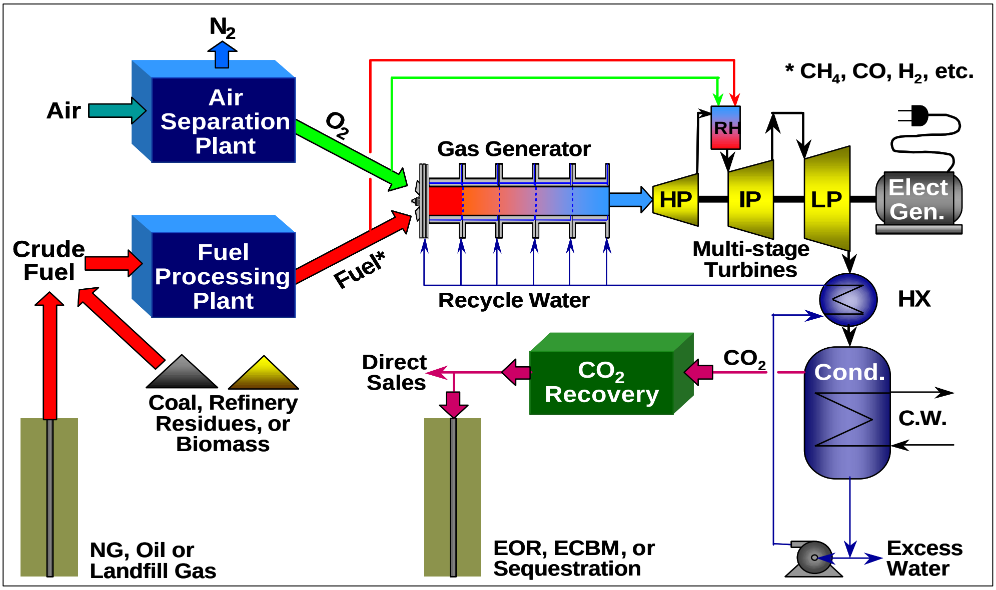
- **Need for cheap O_2 production (cryogenics; O_2 or ion transport through dense ceramic membranes; chemical looping; ceramic auto-thermal recovery(CAR); other)**
- **Need for high efficiencies and cost reductions in the long run by a full integration, especially of an air separation unit and of CO_2 re-use (EOR; ERCBM) and sequestration**
- **Need for R&D,D to demonstrate the concept in a pilot plant by 2015**

FUTURE PROSPECTS

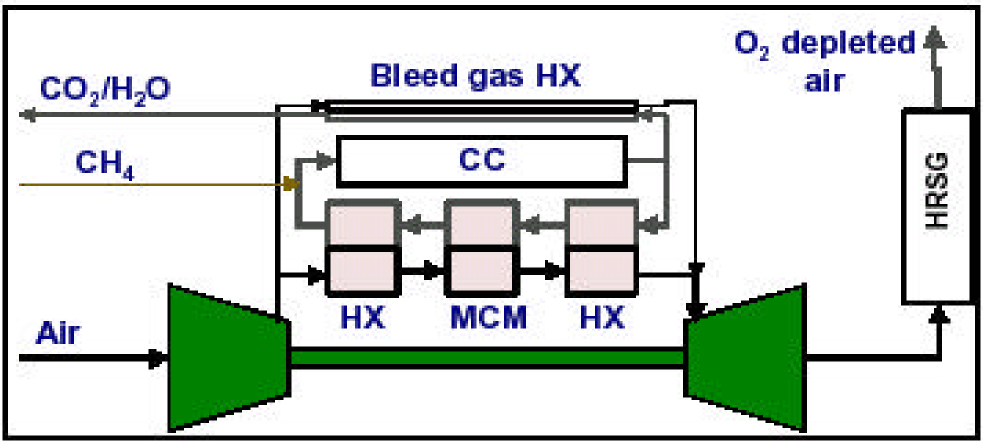
- If BIOMASS (with reforestation) is used in co-combustion or co-gasification in ZEP plants, its carbon is separated and sequestered and is hence withdrawn from the carbon cycle : negative emission
- If a future economy is based on zero emission energy systems and uses H_2 as an energy carrier, it has to be produced free of carbon, for instance by water electrolysis using zero emission plants (renewable energy, hydropower, nuclear energy, ZEPP), Then O_2 is simultaneously generated as a by-product.

  The real issue is to produce cheap and clean H_2
- High temperature fuel cells SOFC, renewable energies and sequestration technologies may be integrated in ZEP gas cycles, increasing efficiency and power output; but cost is currently prohibitive for fuel cells

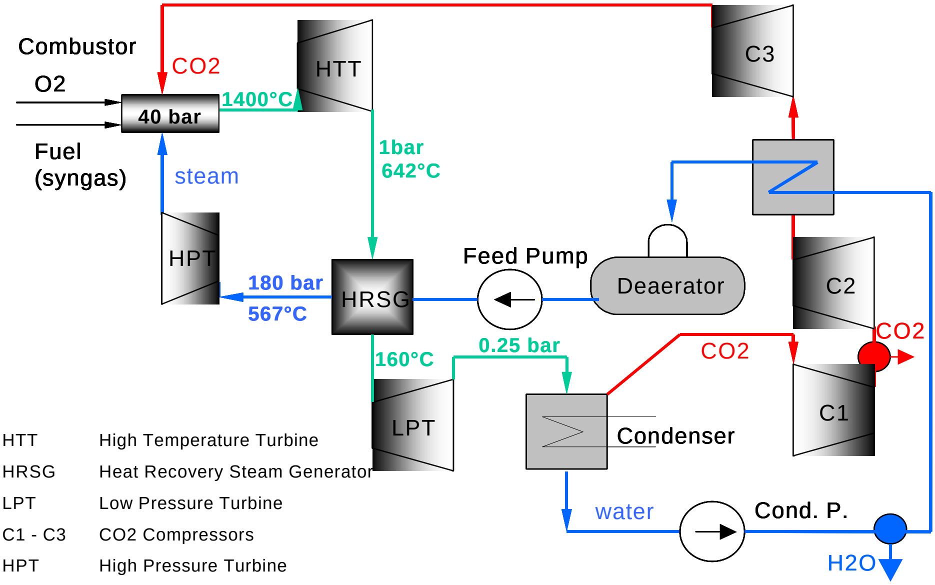
The CES Process



Advances Zero Emission Power (AZEP) Process



Graz Cycle



HTT	High Temperature Turbine
HRSG	Heat Recovery Steam Generator
LPT	Low Pressure Turbine
C1 - C3	CO2 Compressors
HPT	High Pressure Turbine