EMISSION CONTROL IN COMBUSTON PROCESSES

A great success story ..

What about NOx emissions: Are we done yet?

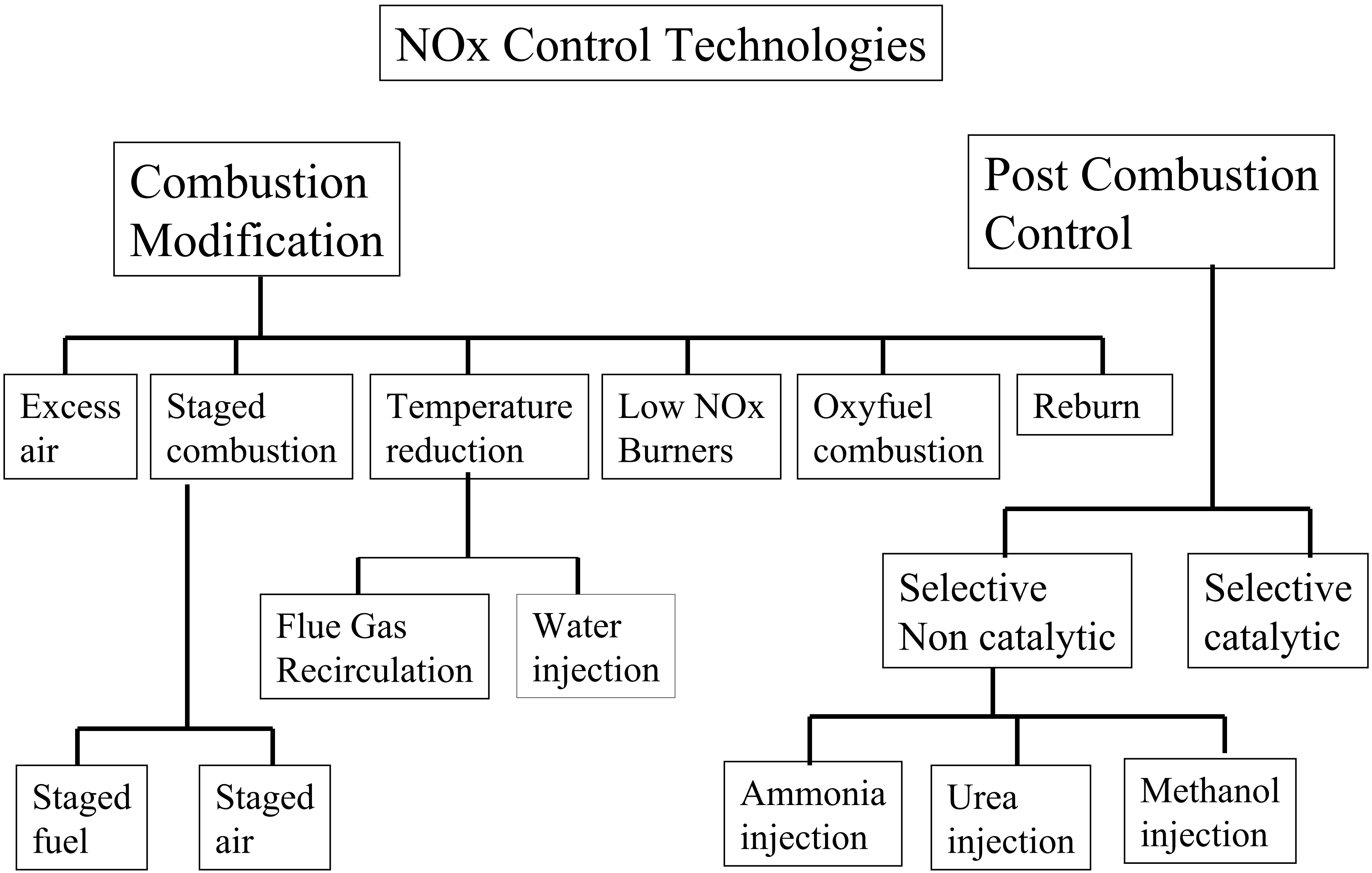
EMISSION LIMITS FOR GROUND BASED GAS TURBINES			
Country	NO_x (at 15% O_2)	CO (at 15% O_2)	Rate Power
ECC	25 vppm	Not stated	> 50 MWth
Italy	29 vppm	48 vppm	> 50 MWth
France	40 vppm	80 vppm	> 20 MWth
Japan (Tokyo)	28 vppm	No limits	Not stated
United Kingdom	28 vppm	80 vppm	> 50 MWth
USA (California)	9 ppm	Not stated	Not stated

Figure by MIT OCW.

- In California's standard for BACT: NOx from GT is limited to 5 ppmvd for simple cycle and 2.5 in combined cycle.
- Mass DEP's is 2 ppmvd for CC and CoGen.
- CO may become more challenging …

NOx Reduction Technologies

- Steam/water injection: lowers T and NO, but may increases CO.
- Flue gas recirculation: lower power density.
- Flameless Combustion.
- Staged Burning: successful especially for high fuel bound N.
- DLN combustors: suffers from instability especially at *part load*.
- Actively controlled combustors: Complex technology.
- Catalytic combustion: …... Under consideration


NOx Control Technologies
Combustion Modification
Post Combustion Control
Excess air
Staged combustion
Temperature reduction
Low NOx Burners
Oxyfuel combustion
Reburn
Flue Gas Recirculation
Water injection
Selective Non catalytic
Selective catalytic
Staged fuel
Staged air
Ammonia injection
Urea injection
Methanol injection

Under lean conditions and at low temperature, CO can become an issue:

Graph removed for copyright reasons. Figure 7 in Docquier, N., and S. Candel. "Progress in Energy and Combustion." *Science* 28 (2002) 107-150.

Use of FGR, Partial Reformer* For NOx Reduction

Diagram and graph removed for copyright reasons.

Cheng et al., LBNL

* Similarity to HCCI

Hydrogen Enrichment:

Burn below nominal flammability limits: ultra lean burn

Diagram and graph removed for copyright reasons.

Miyasato, UCI, LPT&C, 2000

After Treatment Technologies:
Used to guarantee single digit NOx

- SCR: $$4NO + 4NH_3 + O_2 \xrightarrow{600<T<800K+Catalysis} 4N_2 + 6H_2O$$

  More expensive high T catalyst is available for simple cycle (for NG).
  Does not deal with CO, which may be low anyway.

- SNCR: $$4NO + 4CH(NH_2)_{2aq} + O2 \xrightarrow{T\sim 1000C} 4N_2 + 2CO_2 + 2H_2O$$

  Generally more expensive material….

- SCONOx,

$$[K_2CO_3 + NO + CO]_{surface} + ... \xrightarrow{450<T<600K+Catalysis} [KNO_2 + KNO_3]_{absorbed} + CO_2 + ...$$

$$[KNO_2, KNO_3]_{absorbed} + H_2 \xrightarrow{injected\ periodically} [K_2CO_3 + H_2O + N_2]$$

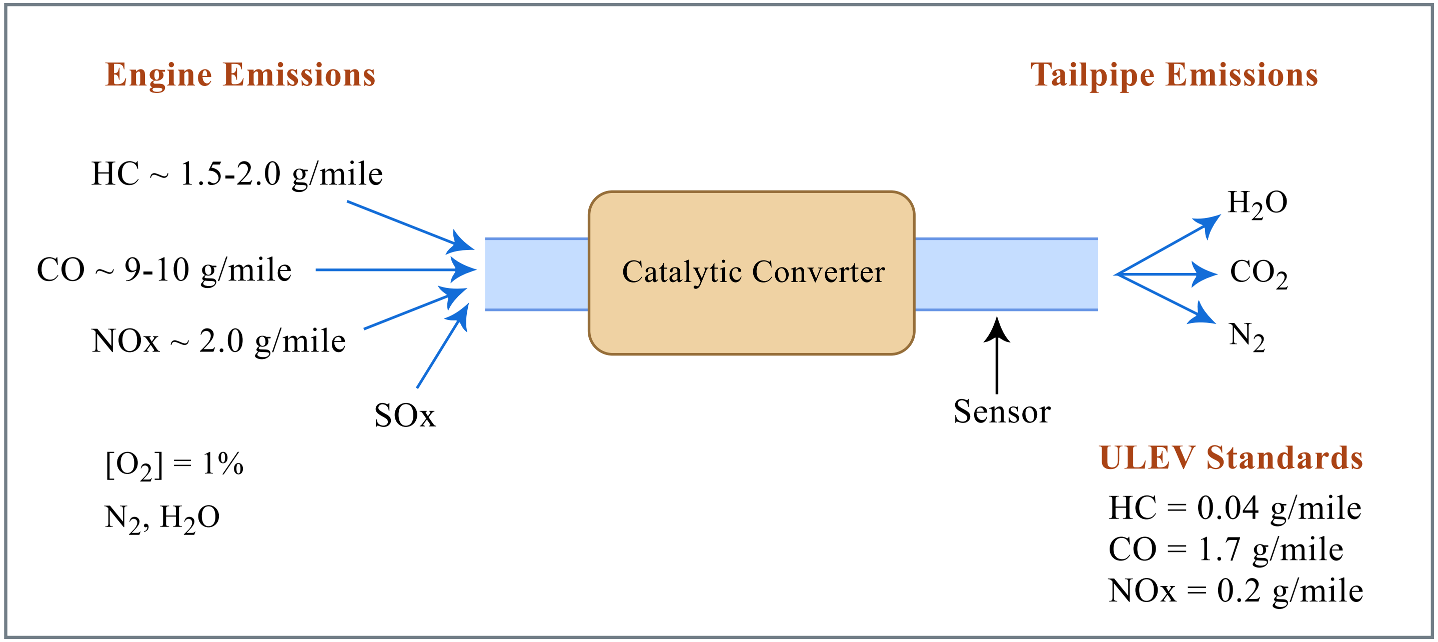
newer, expensive, more effective for NOx and CO (for NG).

Facility schematic removed for copyright reasons.

IC Engines Emissions

PRESENT AND FUTURE AUTOMOTIVE EMISSION LIMITS			
Regulation	HC	CO	NO_x
ULEV* (g/mile)	0.04	1.7	0.2
SULEV* (2003) (g/mile)	0.01	1.0	0.02
EU III** (2000) (g/km)	0.2	2.3	0.15
EU IV** (2005) (g/km)	0.1	1.0	0.08

* FTP-test.
** EU III testcycle.



Figures by MIT OCW.

THE CO_2 PROBLEM IN POWER PLANTS

Kyoto Protocol:

Conceived Dec 1997

Reduce CO_2 emissions to 5.2% below 1990's level ..

To be enforced as of Feb 16, 2005, *today*

Developed nations only: 12.5% in the UK, 8% in the EU, 6% in Japan, 7% in the US (not ratified) …

That leaves China and India, etc.

FutureGen:

$1B, by 2020.

275 MW, burning coal, 60% efficient.

90% CO_2 sequestration

Facility schematic removed for copyright reasons.

AZEP: Advanced Zero Emission Plant

Utilizing membrane reactor for oxy-fuel combustion.

General Guideline for Capture:

- Must achieve highest possible power plant efficiency first.
- If efficiency reduction due to CO_2 capture is high, it will counter the original objective, at a high cost.
- CO_2 should be removed from streams with highest concentration. Amount is important, it is fuel dependent.
- Removing CO_2 from products of C/air combustion after expansion is less efficient, especially for coal.
- Removing N_2 before combustion helps, but this requires CO_2 turbines, or H_2 turbines/fuel cells.

LIFE CYCLE ASSESSMENT (LCA) AND EXERGETIC LIFE CYCLE ASSESSMENT (ELCA) OF AN INNOVATIVE ENERGY CYCLE WITH ZERO CO_2 EMISSIONS

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(1) chemical scrubbing of CO2 from exhaust, 15% efficiency penalty,
(2) burning with O2 first, 11% penalty,
(3) IGCC, burn in O2, separate and then burn H2, least penalty, under development

Facility schematic removed for copyright reasons.

Grouping the Methods of CO_2 Capture

- In **Process Family I**, CO_2 is removed from synthesis gases, which are produced through coal gasification or steam reforming of natural gas. For CO_2 capture, the CO in the synthesis gas must be converted into CO_2 and H_2 through CO conversion with the addition of steam. Following CO_2/H_2 separation, the hydrogen-rich fuel gas undergoes combustion with air in a gas turbine, subsequent to which the CO_2 is disposed of.

- **Process Family II (CO_2 enrichment)** comprises all those processes, in which exhaust gas consisting of CO_2 and steam is produced through combustion in an atmosphere of oxygen and recirculated flue gas or steam. In cycles with CO_2 condensation, liquid CO_2 can be separated without further CO_2 liquefaction.

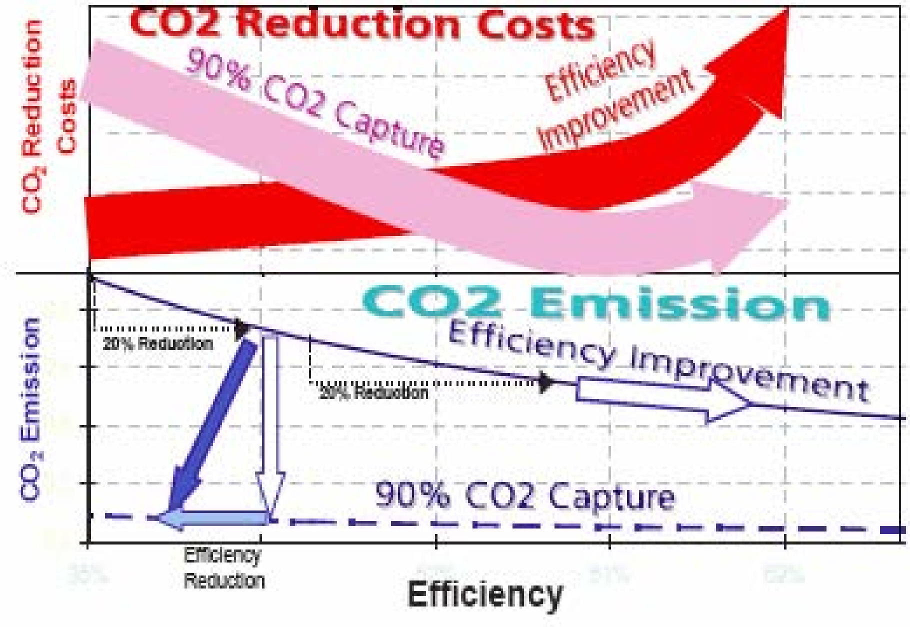
- **Process Family III** includes all those combinations of power plant processes in which CO_2 is removed from the flue gas at the cold end.

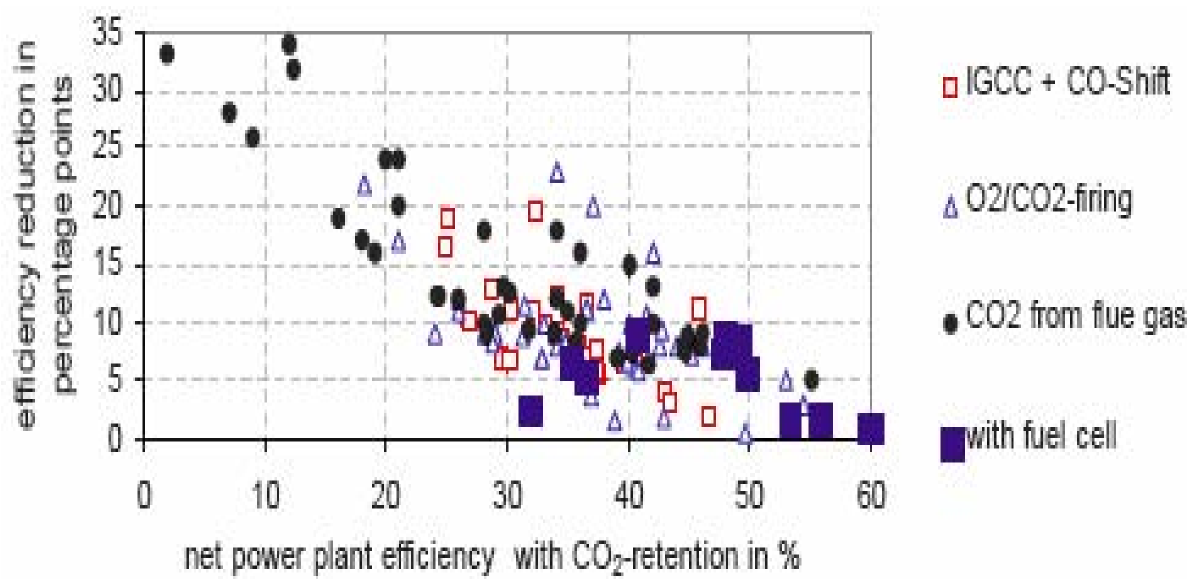
- **Process Family IV** comprises processes such as the so-called hydrocarb process, in which carbon is removed from the fuel prior to combustion.

- **Process Family V** deals with CO_2 capture in power plants with fuel cells, which can be operated with combustible gases of fossil origin.

Gottlicher. "The Energetics of Carbon Dioxide Capture in Power Plants." *DOE* 2004.

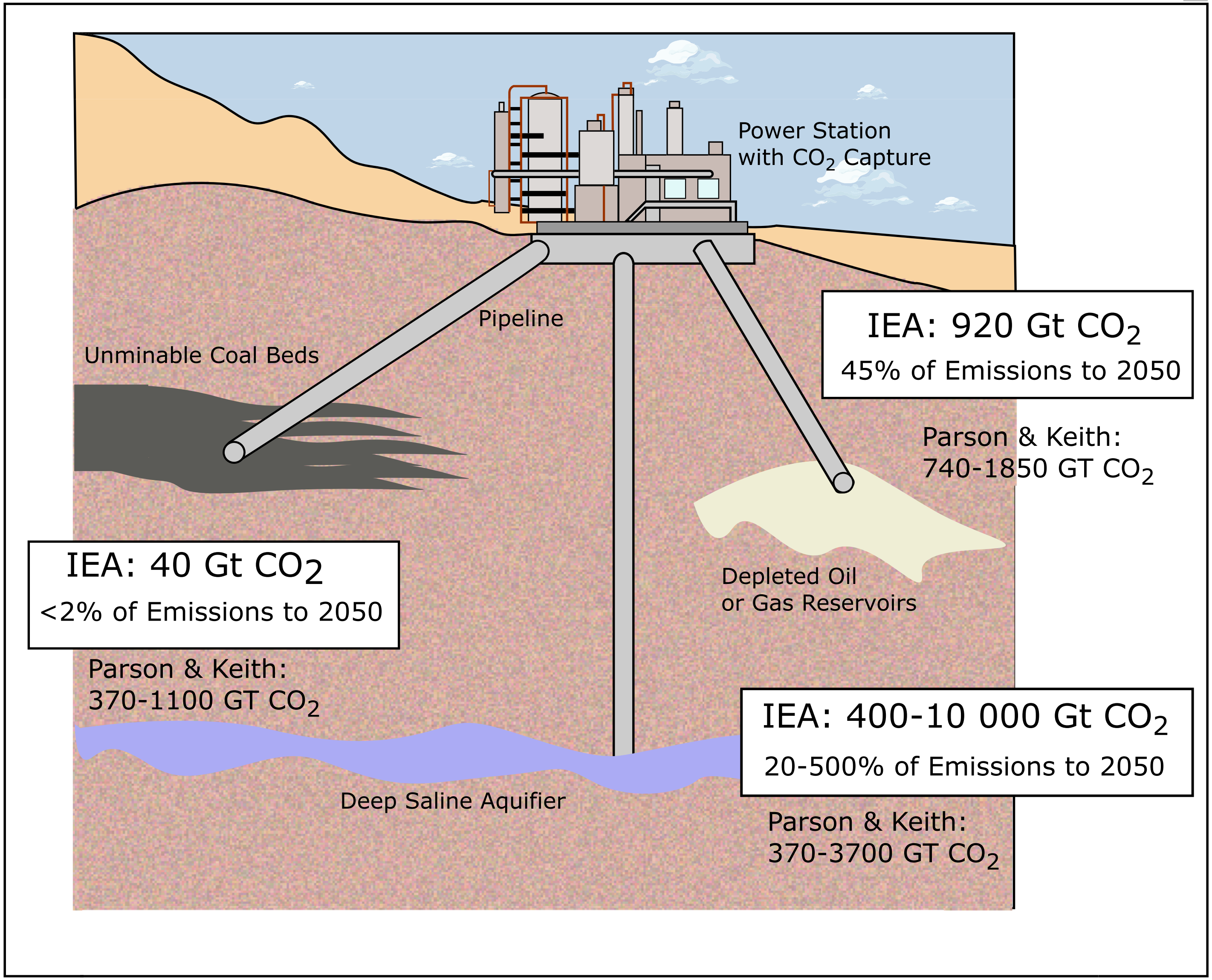
CO2 Reduction via Higher Efficiency and Capture





Gottlicher, The Energetics of Carbon Dioxide Capture in Power Plants, DOE, 2004

Sequestration Potential for CO_2



Source: Freund, IEA - Comparative potentials at storage costs of up to \$20/t CO_2

Source: Parson & Keith, Science 282, 1053-1054, 1998

Figure by MIT OCW.

FUEL CELLS

What do they have to do with fossil?

PEMFC, where does H2 come from?
DMFC, why methanol, or for that matter ethanol
SPFC, how about using methane?

Higher Efficiency: the Fuel Cell

Low T

PEMFC

Proton Exchange Membrane

(polymer electrolyte membrane)

Two schematics removed for copyright reasons.

Electrochemical Analysis Tools

Ideal Efficiency:

$$\eta_{electrochemical} = \left|\frac{\Delta G_r}{\Delta H_r}\right| = \left|\frac{nF\varepsilon}{\Delta H_r}\right|$$

$$\Delta G = (h - Ts)_{H_2O} - \left((h - Ts)_{H_2} - 0.5(h - Ts)_{O_2}\right) \qquad \Delta H = (h)_{H_2O} - \left((h)_{H_2} - 0.5(h)_{O_2}\right)$$

Ideal Voltage (zero current), dependence on pressures:

$$\varepsilon_{H_2} = \varepsilon_0 + \frac{RT}{2F}\ln\left(\frac{p_{H_2} p_{O_2}^{\frac{1}{2}}}{p_{H_2O}}\right) \qquad \varepsilon_0 = \frac{-\Delta G}{2F}$$

Overpotentials: kinetic + Ohmic + transport

$$\eta_a^{anode} = \frac{-RT}{(1-\alpha)nF}\ln\left(i/i_0\right) \qquad \eta_a^{cathode} = \frac{RT}{\alpha nF}\ln\left(i/i_0\right)$$

Real Efficiencies:

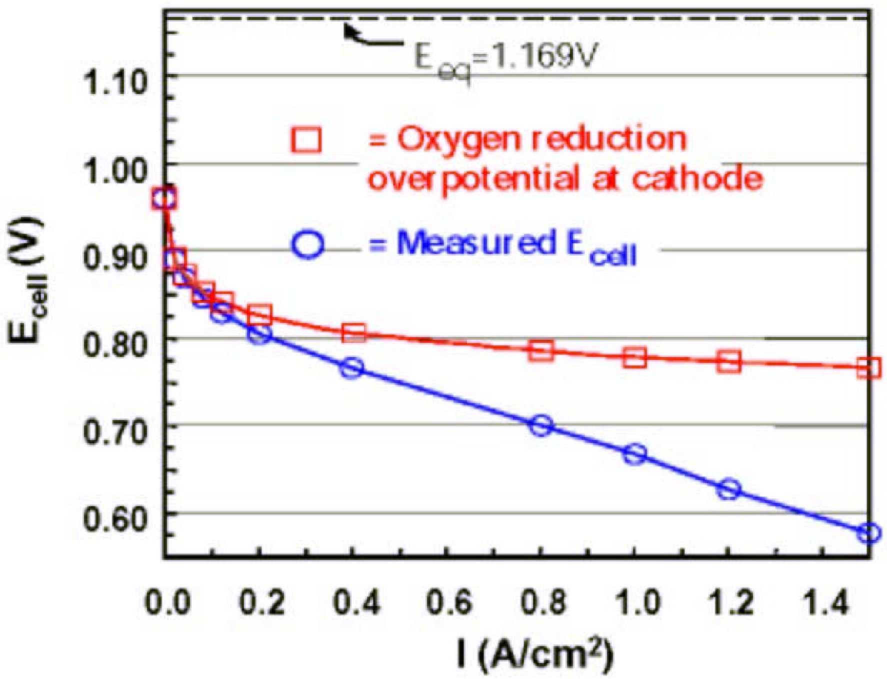


Figure 10 (Lower curve) Cell Voltage (E_{cell}) of a State-of-the-art H_2/Air Membrane Electrode Assembly Operated at 80°C versus the Current Drawn from the Cell (in amp/cm^2) (Gasteiger and Mathias 2002) (The equilibrium [theoretical] cell voltage [1.169 V] is shown by the dashed line at the top of the figure.) (Upper curve) Reduction from the Theoretical Value Caused by the Oxygen Reduction Overpotential at the Cathode Alone (Note that the overpotential is large at all but the very lowest currents. The remaining loss in potential at a given current is caused by internal resistance in the cell and to O_2 gas transport limitations through the air in the porous cathode composite.)

Why is it expensive?

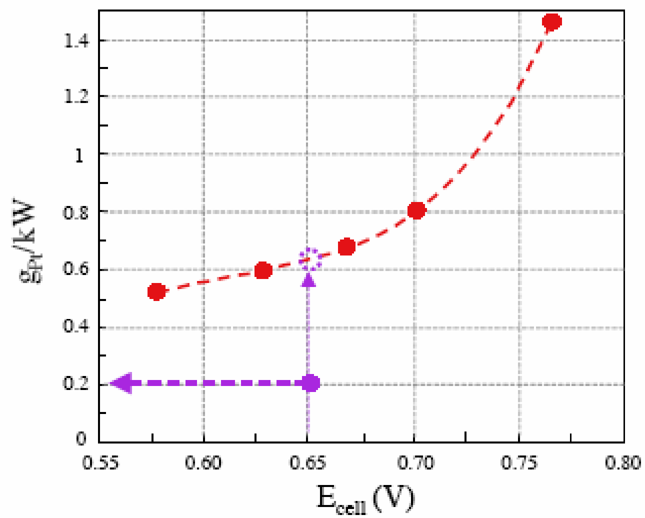


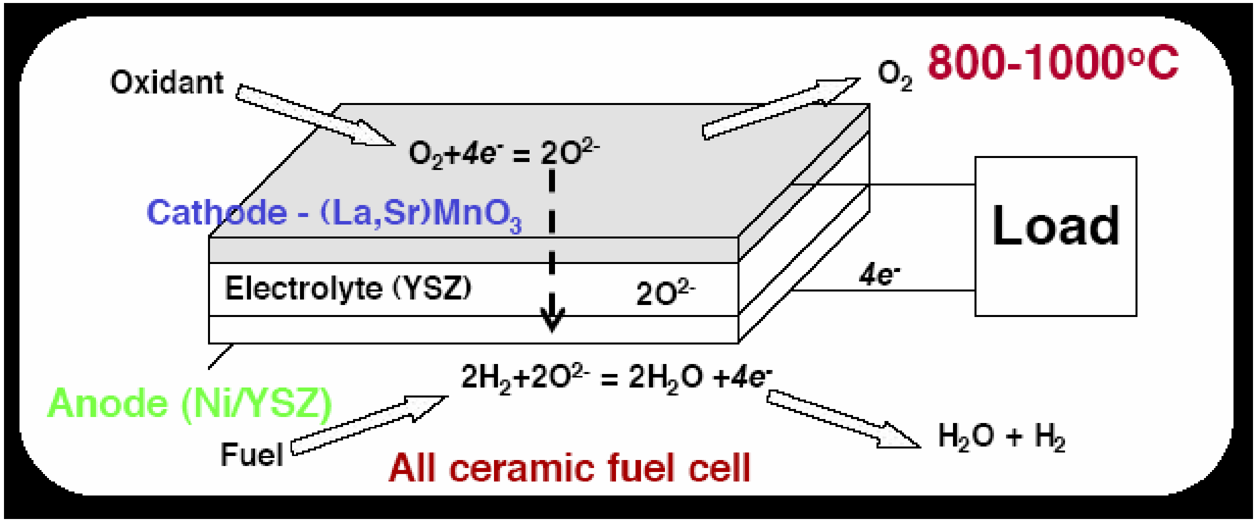
Figure 11 Mass of Pt Used in the Fuel Cell — a Critical Cost Issue (This plot shows the power density per gram of Pt that can be obtained in a state-of-the-art H_2/air membrane electrode assembly operated at 80°C at different operating cell potentials. The present design is to operate at a cell potential of 0.65 V, which must use about 0.65 g of Pt nanoparticles to attain a power output of 1 kW. For cost, weight, and volume reasons, the Pt loading must be decreased to about 0.2 g of Pt/kW output [Gasteiger and Mathias 2002].)

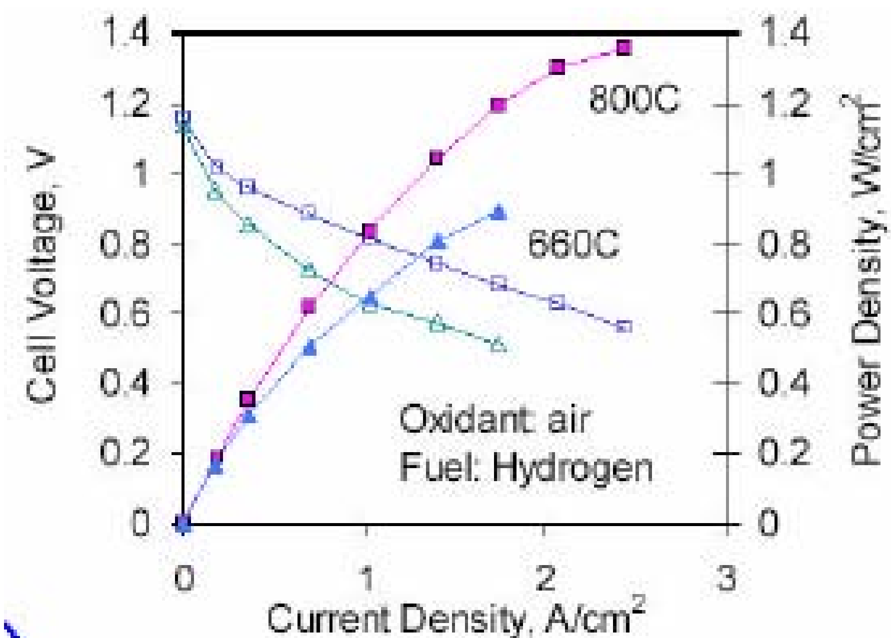
Table 4 Fuel Cell Types and Their Operating Features

Fuel Cell Type	Electrolyte	Conducting Ion	Temperature (°C)	Features
Polymer	$CF(CF_2)_nOCF_2SO_3^{2-}$	H^+ (hydrated)	60–80	High power density, Pt catalyst, must be kept wet, poisoned by CO
Alkaline	KOH	OH^-	90	High power density, cannot tolerate CO_2
Phosphoric acid	H_3PO_4	H^+	200	Medium power density, Pt catalyst, sensitive to CO
Molten carbonate	Li_2CO_3 / K_2CO_3	CO_3^{2-}	650	Low power density, Ni catalyst, needs CO_2 recycle
Solid oxide	$Zr_{0.92}Y_{0.08}O_{1.96}$	O^{2-}	700–1,000	Medium-to-high power density, accepts CO as fuel
Direct methanol	$CF(CF_2)_nOCF_2SO_3^-$	H^+ (H_2O, CH_3OH)	60–120	Medium power density, low efficiency, high Pt content

[a] Source: Kumar (2003).

Solid Oxide Fuel Cells hold more promise because of high T … ,





Combined Nernst and overpotential efficiency 40-50% close to peak power …

Courtesy of U.S. DOE.

High-Temperature SOFC Combined Cycle:

fuel cell characteristics +
after burner/combustor +
steam or gas turbine cycle

claimed η > 65% by harvesting the thermal energy in the exhaust ….. ?

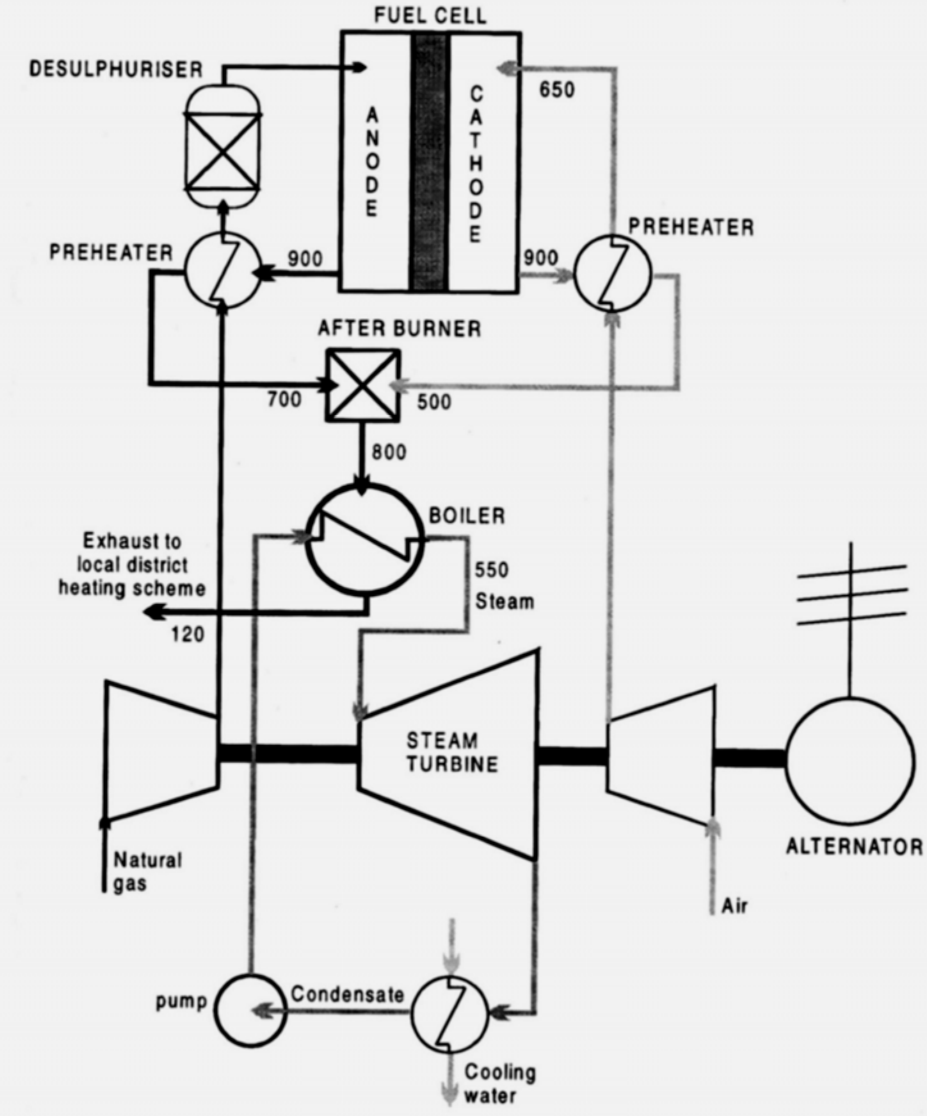
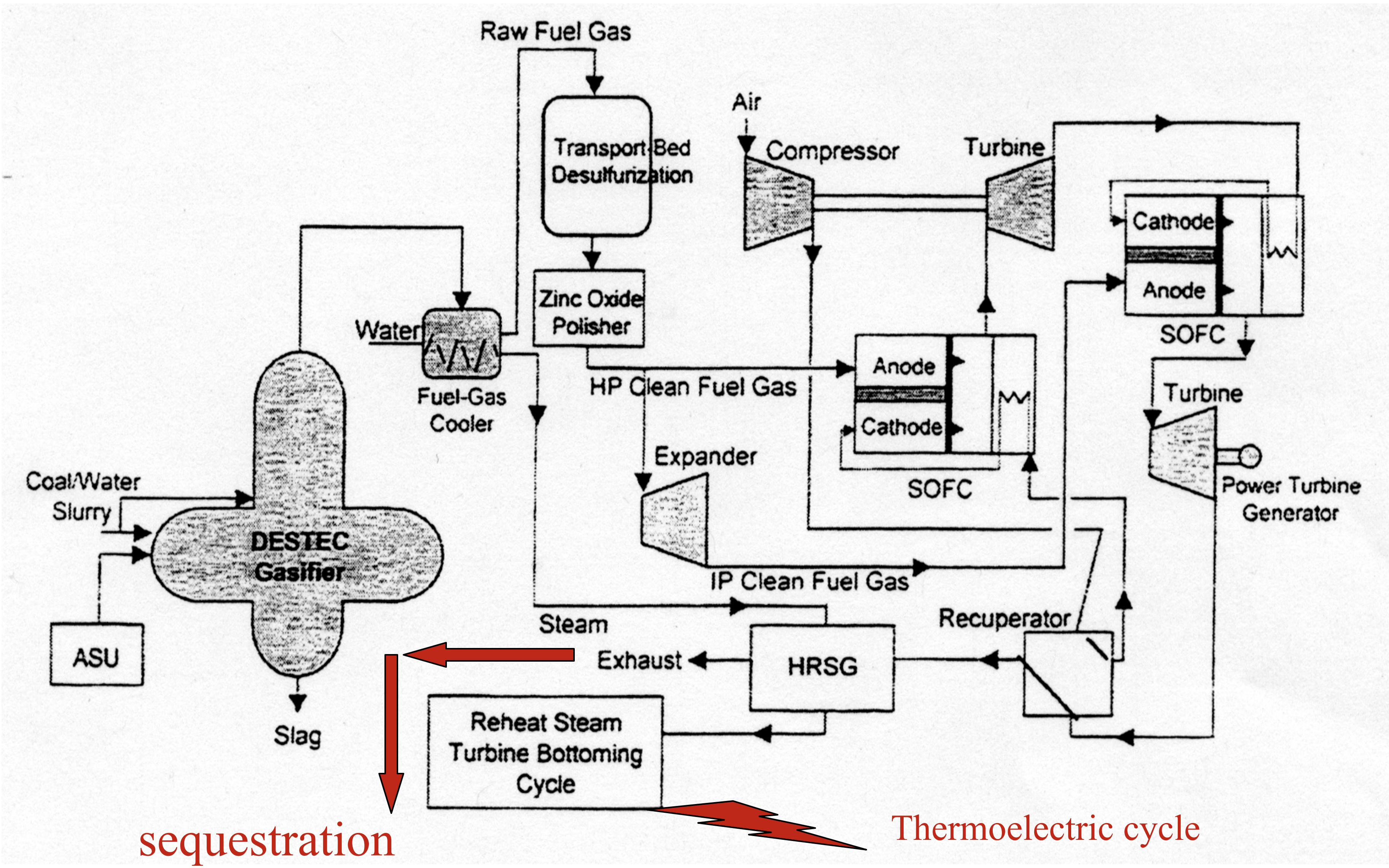


Figure 6.3 Diagram of a possible SOFC and steam turbine combined cycle. The figures indicate likely approximate temperatures of the fluids, in Celsius, at the different stages of the process.

Courtesy of U.S. DOE.

DOE Vision 21: The Cascading Cycle
Gasification/Fuel Cell/Gas Turbine/Steam Turbine Cycle



David Tucker, 2002, NETL and Sandian N. Labs