# REDUCTION OF CARBON DIOXIDE EMISSIONS BY CAPTURE AND RE-INJECTION

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## ABSTRACT

The carbon dioxide concentration in atmosphere has a disquieting effect on climate and a strong reduction of the $CO_2$ anthropogenic emissions appears henceforth necessary. It can be done by reducing energy consumption, by improving energy efficiency, and by using fuels or energy with a lower carbon content; it will nevertheless be necessary to capture and secure store a part of emitted CO2. That will mainly imply to extract the CO2 included but diluted in the combustion flue gases and to concentrate them in order to optimize the storage volume, but this operation of CO2 « capture » is very penalizing and will lead to important change in energy conversion processes (steam or power generation). Separate nitrogen from air before combustion is an attractive way for producing concentrated flue gases, ready for re-injection and pilot projects of oxy-boilers are launched this year in Germany and in France.

**Keywords: Carbon dioxide Emissions, Carbon Capture, Oxy-combustion**

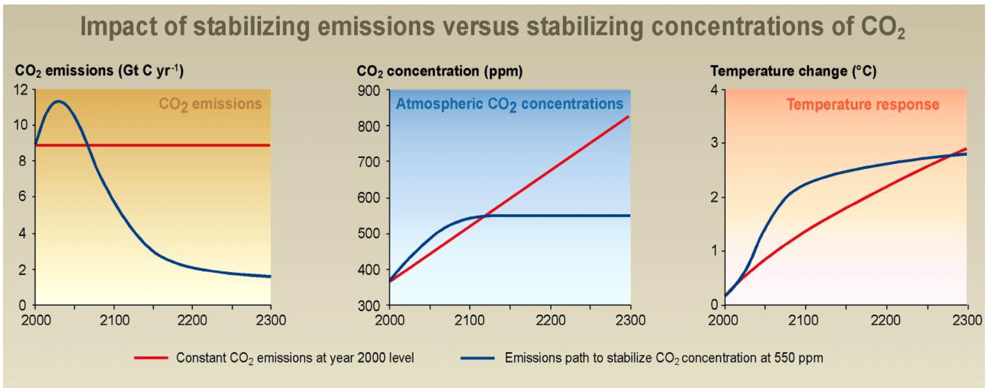
## Introduction

The world-wide economy and energy consumption are growing rapidly and lead to a noticeable increase of carbon dioxide concentration in atmosphere, with a disquieting effect on environment and climate. There is now enough evidence of a link between the increase of greenhouse gas (GHG) concentration in the atmosphere and the measured temperature rises; it is clearly shown by the analysis of the Vostock ice core with an history of 400,000 years. Impact of the CO2 anthropogenic emissions on environment is now also recognized, even if it remains difficult to quantify it.

CO2 contributes to 90% of GHG emissions and anthropogenic CO2 is probably responsible for more than 60% of the growth of these emissions (80% in the EU); most of them are provided by fossil fuel combustion for energy conversion and utilization. Primary energy consumption is mainly based on fossil fuels (83% in the World in 2000) which will remain the principal energy source in 2030.

Anthropogenic portion of the global carbon cycle seems to be relatively small but impact on climate will be strong if CO2 concentration in atmosphere is not stabilized.

Stabilizing CO2 emissions at present level will not cope with a stabilization of CO2 concentration in atmosphere and a drastic reduction of CO2 emissions will be necessary as it can be seen here-below (*Fig. 1.*)[1].



*Source: IPCC SRCCS*

Fig. 1. *Impact of stabilizing emissions versus stabilizing concentrations of* $CO_2$.

## Reduction of CO2 Emissions

A drastic reduction of the GHG emissions has been decided in the framework of the Kyoto agreements and CO2 is the main GHG targeted by the protocol. It will imply strong energy savings and the capture and geological storage of a significant part of the emitted CO2.

A large reduction of these emissions, at the world scale, can be done at first by reducing energy consumption and improving energy efficiency, then by using fuels or energy with a lower carbon content, and finally by capture and storage of part of emitted CO2.

### Contribution of Industry

More than half (55%) of global CO2 emissions are produced by power plants and heavy industry - mainly petroleum, cement and steel industries – and actions on them emissions will have a major impact on the global emissions.

Efficient actions can be done in the industrial activity, through a better control of emissions with reliable emissions figures (using reporting guides, external checking), by the reduction or interdiction of some disposals (associated gas flarings, N2O and HFC emissions), by improving energy efficiency, and also with introduction of penalties on CO2 disposal.

*Improvement of energy efficiency in Industry* may be done at all levels, from conception and design of industrial sites to their operation, including selection of processes and equipment and integration of utilities; a good information and sensitization of operators based on an energy referential accessible to all actors (i.e. energy efficiency index in reference to an « ideal » operation case) will help to optimize the working parameters.

### Evolution of energy system

#### - *with fossil fuels*

In regard on the present estimation of the World reserves, coal, non conventional oil and natural gas will take a growing part of fossil fuels production in the future, which will induce a higher spread of fossil fuels characteristics in the future (Lhv, CO2 emissivity…).

Growth of energy resources implies to increase the exploitation of coal reserves and of non conventional petroleum resources such as the extra-heavy crude fields which are important. Sustainable development of these reserves raises the problem of CO2 pollution associated with the valorisation of coal and petroleum residues, as well for steam or power generation (« steam-coal »), as for the production of synthetic hydrocarbons or fuels (coal-to-liquid route), due to a lower hydrogen content or the presence of impurities to eliminate.

Gasification process allows conversion of any fossil fuel into fuel source to users or petrochemical products and appears particularly as a key process for energy conversion, as hydrogen will probably be a major energy carrier in the future : hydrogen appears to many as the clean fuel of the future, because its only by-product is water. However hydrogen is not a primary fuel source. Like electricity, it is a mean of transmitting energy from primary fuel sources to users. Like electrical power, hydrogen must be produced and transported, although hydrogen has an additional attribute that makes it more attractive for some applications than electricity : it can be stored for later use. This feature makes it useful for powering vehicles and other portable devices.

Primary energy conversion is also a source of CO2 emissions, due to a limited thermal efficiency of conversion in the present state of the art : between 40 and 58% for large power generation, depending on the fuel and the process; a local thermal use of the produced steam may noticeably increase this efficiency – till 85% for a Natural Gas Combined cycle with a total LP steam cogeneration – and should be promoted. Oxygen production is still very energy consuming, with a conversion efficiency lower than 35%, and should be improved as oxygen is a key component for gasification and could become also important for oxy-combustion in case of CO2 capture in flue gas.

- *with carbon-free or renewable energies*

Reduction of emissions will imply the development of carbon-free energies (nuclear or hydraulic power) and the merge of more « industrial » renewable energies, such as biomass, eolian and solar power. The mix of energies will also be developed : bi-fuels (or flex-fuels) system, hybrid cars …

## Carbon Capture and Storage (CCS)

Beyond the improvement of energy efficiency, which is the first step, and the resort to less carbonated fuels and energies, the feasibility of long-term $CO_2$ capture and storage appears as another promising issue, particularly the geological storage.

Carbon capture and storage (CCS) can be defined as sequestration of carbon which would otherwise be emitted to, or remain, in the atmosphere.

Its leads at first to re-inject the CO2 already removed from acid gases, concentrated and available under pressure : several projects are launched (at Sleipner and Snohvit in Norway, at In Salah in Algeria,..), but the concerned volumes remain limited.
It will imply also and mainly to extract the CO2 included but diluted (at concentrations in the range of 3 to 14%) in the combustion flue gases and to concentrate them in order to optimize the storage volume, and this operation of CO2 « capture » is very penalizing and will lead to reconsider number of gas treatment processes (or other hydrocarbons).
This is an important point for the future power stations for instance, particularly when burning coal or lignite ; the question rises also presently on new projects of heavy oil hot production where installation of mega-boilers is foreseen for doing massive steam injections.

CCS is a four-step process where: first, a pure or nearly pure stream of $CO_2$ is captured from flue gas or other process stream; next it is compressed to about 100-120 bars; it is then transported to the injection site; and finally, it is injected deep underground into a geological formation such as an oil and gas reservoir where it can be safely stored for thousands of years or longer.

CO2 capture and storage : which concepts ?

Qualification of CO2 sources should be made on the following criteria :

- Large stationary point sources (mainly electricity generation plants, but also petrochemical plants, cement or steel plants)
- High CO2 concentration in the waste, flue gas or by-product stream (purity)
- Pressure of CO2 stream
- Distance from suitable storage sites

Significant storages should be identify such as :

- Stable sedimentary basins already exploited for hydrocarbons
- Hydrocarbon fields (oil and gas, productive countries), with priority to CO2 EOR and EGR if possible
- Saline aquifers (consumer countries)

Minimal costs should be found for the transportation between capture and storage sites, by pipelines or tankers.

Capture of $CO_2$ can be applied to large point sources. The $CO_2$ would then be compressed and transported for storage in geological formations, in the ocean, in mineral carbonates, or for use in industrial processes. Large point sources of $CO_2$ include large fossil fuel or biomass energy facilities, major CO2-emitting industries, natural gas production, synthetic fuel plants and fossil fuel-based hydrogen production plants.

Geological storage can be done in oil or gas fields, saline formations or in coal beds. Ocean storage can be done by direct injection in the water column, or by depositing the CO2 on the sea floor where it will be isolated from the atmosphere longer. Mineral carbonation can in principle also be done, but is still expensive both in terms of costs and of energy use. The CO2 can also be used in industrial facilities, but the potential for CO2 reduction for this is small.

Large stationary CO2 point sources of CO2 include large fossil fuel or biomass energy facilities, major CO2-emitting industries, natural gas production, synthetic fuel plants and fossil fuel-based hydrogen production plants.

Globally, emissions of CO2 from fossil-fuel use in the year 2000 totalled about 23.5 GtCO2/yr (6 GtC/yr). Of this, close to 60% was attributed to large (>0.1 MtCO2/yr) stationary emission sources (*Table 1.*). However, not all of these sources are amenable to CO2 capture. A first target for capture could be sources larger than 0.5-1 MtCO2/year corresponding to 300-500 MWth Lhv.

Currently, the vast majority of large emission sources have CO2 concentrations of less than 15% (in some cases, substantially less). However, a small portion (less than 2%) of the fossil-fuel-based industrial sources have CO2 concentrations in excess of 95%. The high-concentration sources are potential candidates for the early implementation of CCS because only dehydration and compression would be required at the capture stage.

Table 1. Large stationary $CO_2$ point sources.

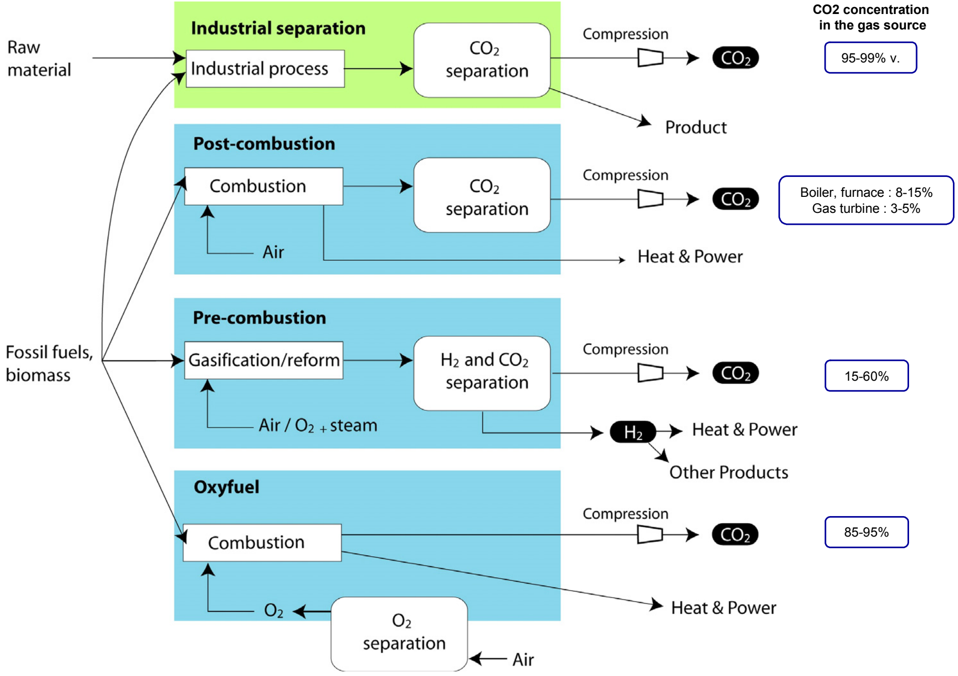
| Process | No. of sources | Emissions ($MtCO_2/yr$) |
|---|---|---|
| **Fossil Fuels** | | |
| Power (coal, gas, oil and others) | 4,942 | 10,539 |
| Cement production | 1,175 | 932 |
| Refineries | 638 | 798 |
| Iron and steel industry | 269 | 646 |
| Petrochemical industry | 470 | 379 |
| Oil and gas processing | N/A | 50 |
| Other sources | 90 | 33 |
| **Biomass** | | |
| Bioethanol and bioenergy | 303 | 91 |
| **Total** | **7,887** | **13,466** |

Source: IPCC Special Report approved September 25th, 2005, on Carbon dioxide Capture and Storage

## Capture processes

There are different types of CO2 capture systems: post-combustion, pre-combustion and oxyfuel combustion as it can be seen here-below (*Fig. 2.*). The concentration of CO2 in the gas stream, the pressure of the gas stream and the fuel type (solid or gas) are important factors in selecting the capture system.

- *Post-combustion capture* of CO2 from the flue gases emitted by combustion equipment or a power plants consists in separation of CO2 from flue gas with a similar technology as the one used in the natural gas processing industry, which operates in a mature market.
- The technology required for *pre-combustion capture* is widely applied for gasification or steam reforming, like in fertilizer manufacturing or in hydrogen production. Although the initial fuel conversion steps of pre-combustion are more elaborate and costly, the higher concentrations of CO2 in the gas stream and the higher pressure make the separation easier.



Source: IPCC SRCCS

Fig. 2. *Capture processes*.

- *Oxyfuel combustion* can be accomplished by using oxygen instead of air to combust the fossil fuels, thereby producing emissions of only $CO_2$ and water, from which the $CO_2$ is easily separated. This results in high CO2 concentrations in the gas stream and, hence, in easier separation of CO2 and also in energy requirements in the separation of oxygen from air. This process is in the demonstration phase using high purity oxygen.

- *Energy requirements for capture* :

The energy requirements is an important point, as it costs energy to capture CO2 from the flue gases of a facility. The net reduction of emissions to the atmosphere through CCS depends on the fraction of CO2 captured, the increased CO2 production resulting from the additional energy required for capture, compression, transport and injection processes, and depends also on any leakage from transport and the fraction of CO2 retained in storage over the long term.

The additional energy use is on the order of 10 to 40%, depending on the fuel and the capture process. In the facility, 85 to 95% of the CO2 would be captured. Taking into account the emissions arising from the extra energy use leads to a net CO2 emission avoidance of 55 to 90%.

## Carbon Storage

Several types of storage are possible :

- *Biomass storage*

Biomass is presently a net source of CO2 emission due to global afforestation; to change it could allow biomass to become globally a CO2 well but meanwhile the global potential of sequestration is limited.

- *Geological storage*

Storage of CO2 in deep, onshore or offshore geological formations uses many of the same technologies that have been developed by the oil and gas industry and has been proven to be economically feasible under specific conditions for oil and gas fields and saline formations, but not yet for storage in unminable coal beds. A coal bed that is unlikely to ever be mined - because it is too deep or too thin - may be potentially used for CO, storage. If subsequently mined, the stored CO2 would be released. Enhanced Coal Bed Methane (ECBM) recovery could potentially increase methane production from coals while simultaneously storing CO2.
If CO2 is injected into suitable saline formations or oil or gas fields, at depths below 800 m, various physical and geochemical trapping mechanisms would prevent it from migrating to the surface. At depths below 800-1,000 m, CO2 becomes supercritical and has a liquid-like density (about 500-800 kg/m3) that provides the potential for efficient utilization of underground storage space and improves storage security. In general, an essential physical trapping mechanism is the presence of a caprock (rock of very low permeability that acts as an upper seal to prevent fluid flow out of a reservoir).
Coal bed storage may take place at shallower depths and relies on the adsorption of CO2 on the coal, but the technical feasibility largely depends on the permeability of the coal bed.
The combination of CO2 storage with Enhanced Oil or Gas Recovery or, potentially, Enhanced Coal Bed Methane recovery (ECBM) could lead to additional revenues from the oil or gas recovery. The produced methane would be used and not released to the atmosphere.
Well-drilling technology, injection technology, computer simulation of storage reservoir performance and monitoring methods from existing applications are being developed further for utilization in the design and operation of geological storage projects. *Problem of long-term reliability and safety to demonstrate by studies and industrial pilot plant.*

- *Ocean storage*

Ocean storage potentially could be done in two ways: by injecting and dissolving CO2 into the water column (typically below 1,000 meters) via a fixed pipeline or a moving ship, or by depositing it via a fixed pipeline or an offshore platform onto the sea floor at depths below 3,000 m, where CO2 is denser than water and is expected to form a "lake" that would delay dissolution of CO2 into the surrounding environment. Ocean storage and its ecological impacts are still in the research phase. But public acceptability is presently very weak.

Feasibility of storage depends on three major technical issues : CO2 injection, CO2 storage capacity, long term CO2 storage, so as on the relevant questions associated to the risk management :

- Can sequestration be reliable ?
- What legislation is applicable ?
- What could be the public perception ?

## CO2 Capture Options

Fossil fuels combustion is the main source of CO2 emission in the Industry. This combustion may be total (heaters, boilers or gas turbines) or partial (gasification with partial oxidation).
Large installations are in project in the world for the on-coming years for steam production or power generation.

Emission sources

Mega-boilers are foreseen for instance in new projects for extra-heavy oil hot production, in Canada or in Venezuela where massive steam injections will be done for allowing oil flowing to a collector pipe ("steam assisted gravity drainage" process as shown on *Figure. 3.*). Steam needs can rise till three volumes of water per volume of product oil. The fuel used for boilers could be a residue of heavy oil upgrader, such as asphalt or petcoke[2].

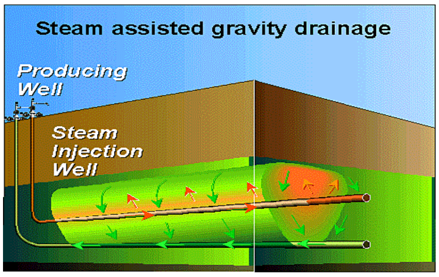


Fig. 3. *Steam assisted gravity drainage for extra-heavy oil hot production.*

Many power plants will be built also in the coming years. Steam or IGCC power plants have been strongly improved in the last years and are still in progress with a thermal efficiency which will be higher than 50% by 2020[3]; global energy efficiency will have progressed of nearly 20% between 1992 and 2020. Impact of capture on these plants will reduce their efficiency of about 15%, but resulting efficiency will remain above the values of 1992 (without capture).

Quality of CO2 source – concentration or pressure - depends on the used process as written above; specification of CO2 to be re-injected will depend on the required specification for the chosen geological storage (type, size, pressure) and on possible options like CO2 use for E.O.R. or on a possible CO2 – SO2 re-injection.

## Capture options

- *Direct capture of CO2 in flue gas* (*Fig. 4.*) with a chemical solvent like MEA is presently considered as a reference[4] for amine is a well-known process (CO2 capture rate, duty) and this capture process may be installed downstream an existing combustion plant, but costs and energy demands are high.

This process consists on the separation of CO2 from flue gas by scrubbing them using an amine solution; After leaving the scrubber, the amine is heated to release high purity CO2 and the CO2-free amine is then recycled. Powerful solvents must be used to capture CO2 meaning that a large amount of energy is then needed to release the carbon dioxide.

Energy required is about 2 tons of steam per ton of CO2, or 4GJ/t CO2, which corresponds to 25-35% of combustion energy upstream the flue gas.

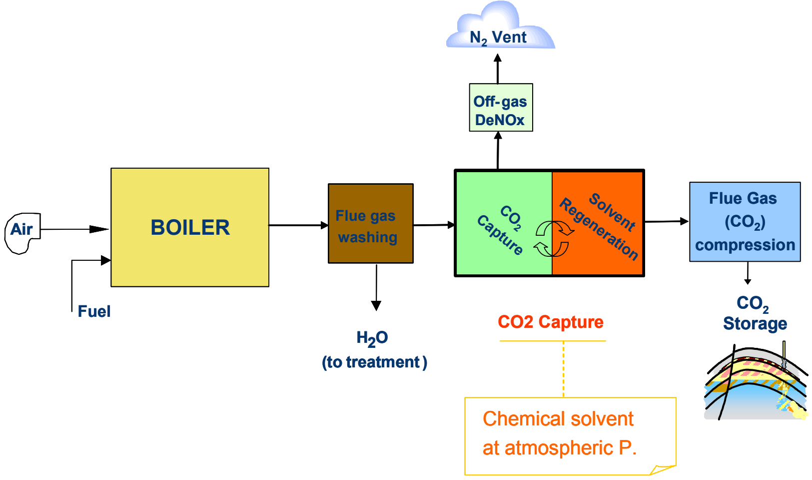


Fig. 4. *$CO_2$ Capture in flue gas.*

- In *pre-combustion capture*, between gasification and H2 combustion, a water shift is used for converting the syngas into an H2-CO2 mixture; physical solvents are used for separation of CO2, with the advantage that it can be released mainly by depressurization, thus avoiding the high heat consumption of amine scrubbing processes.

- With *oxy-combustion* (*Fig. 5.*) the flue gas has a high CO2 concentration - typically greater than 90% - but obtention of oxygen is energy penalizing and research effort is done for the development of more efficient oxygen separation process, using ceramic membranes. An alternative combustion process using a metal oxide in chemical looping is also on-study and could be promising in the long-term.

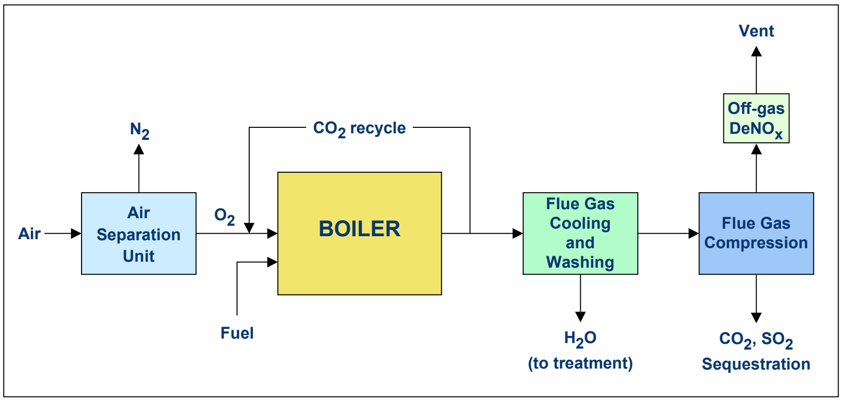


Fig. 5. *Oxy-combustion simplified flowsheet.*

CCS cost estimate

Costs for the various components of a CCS system vary widely, depending on the reference plant and the wide range in CO2 source, transport and storage situations. In most CCS systems, the cost of capture (including compression) is the major component and is estimated between 40 and 60 US$/tCO2.
Transportation of 1-5 MtCO2/year over 100 km costs between 1 and 4 US$/tCO2.
Geological storage costs vary between 2 and 8 US$ per ton stored and excludes monitoring costs of 0.1 to 0.3 US$/tCO2.

With the best available technologies the total cost of the CCS system is estimated between 40 and 80 $/tCO2 with a capture cost of about two third of the total.

It should be observed that the present data are based on energy prices in 2003 with oil prices of 15–20 US$ per barrel, and are used in the main on-going international projects. Increases in market prices of fuels used for steam or power generation would generally tend to increase the cost of CCS. The quantitative impact of oil price on CCS is uncertain, but increase of CCS cost could reach one third of oil price increase.
However, revenue from EOR would generally be higher with higher oil prices.
Retrofitting existing plants with CO2 capture is expected to lead to higher costs and significantly reduced overall efficiencies than for newly built power plants with capture.

Over the next decade, the cost of capture could be reduced by 20–30% (without consideration of fuel price change), and more should be achievable by new technologies that are still in the research or demonstration phase. The costs of transport and storage of CO2 could decrease slowly as the technology matures further and the scale increases.

## The Oxy-combustion route

Separate nitrogen from air before combustion is an attractive way for producing concentrated flue gases, ready for re-injection and pilot projects of oxy-boilers are launched this year (at Schwarze Pumpe in Germany, at Lacq in France). This merging route appears very promising.

Technologies

For *air separation*, cryogenic distillation is presently the most economical process for large scale production with a power consumption of approximately 220 kWh/t of oxygen supplied at low pressure at boiler inlet. New technology using ceramic autothermal recovery reactor (CAR) is presently on study.

Process and operation of an *oxy-fired boiler* are very similar to those of an air–fired boiler, with a recycle rate of flue gas (~70%) adapted to safety constraint, with a specific “oxygen” design if oxygen content is higher than 30% and an acceptable thermal flux on boiler tubes.

*Flue gas treatment* should be designed in consideration of specification of CO2 for injection, with possibly a CO2 – SO2 co-injection and a non-condensable gas content to define. Acid condensates issued from the flue gas cooling should be treated for disposal; a minimum of two stages will be necessary for inert gas separation from the liquid CO2 before its transportation to the injection site.

Experimentation on pilot plants

The Swedish power company *Vattenfall,* which owns mines and power stations in Germany, has studied the feasibility of an oxy-boiler for a steam power plant[5] and has decided in March 2005 to built a pilot plant for a " CO2 free power station" next to the *Schwarze Pumpe* coal-fired power station in Brandenburg, in the south of Berlin. The pilot will fire lignite or brown coal, which is one of eastern Germany's primary mineral resources, with a fuel output of 30 MW and use pure O2 and CO2 recycle technology. It will be built in 3 years for a commissioning expected in 2008 with a 2 years test program.
Storage site is foreseen at Schweinrich, at 250 kilometers from Schwarze Pumpe.

The French energy company *Total* has decided in September 2005 to convert an existing thermal boiler producing 50 t/h of 60 bar steam (50 MWth) to an oxy-fired combustion boiler with flue gas recycle in the *Lacq* gas plant, in south-west of France. The pilot will fire various fuels including sour heavy crude with a high sulfur content (6% wt) and demonstration of non-condensable gas separation and CO2 liquefaction will be made. Global objective is to demonstrate the industrial and regular feasibility of a whole capture, injection and geological storage chain of CO2 (or CO2+SO2) and its economical interest for steam production by oxy-combustion.
Start-up is foreseen in 2008 and HP liquid CO2 will be injected in a nearby depleted reservoir, presently on study.

## Conclusions

A limitation of climate change at an acceptable level will require a strong reduction of fossil fuels consumption as a priority, particularly in transportation and habitation, where emitted carbon cannot be captured ; capture and storage of a large part of carbon issued from industrial combustion will help to reduce emissions, but will be only part of the solution.

Time has probably come now to imagine and validate a new economic development model, which associate growth and environment management.

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