

## ZERO CARBON POWER GENERATION: IGCC AS THE PREMIUM OPTION

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### Abstract

The idea of capturing carbon dioxide from flue gases is not new. First commercial applications were realized in the field of Enhanced Oil Recovery (USA, 1977 – 1984). CO<sub>2</sub> has been injected in the oil reservoirs to increase the mobility of oil.

Historically, its origins were not related to green house gases (GHG) effect. It was not before 1996, when the first commercial CO<sub>2</sub> capture with sequestration motivated by GHG reduction was realized. In 1996 Statoil of Norway began injecting CO<sub>2</sub> beneath the bottom of the North Sea. The stiff Norwegian carbon tax was the strong incentive in this pioneering project.

In this Paper the role of gasification and specifically the role of IGCC (Integrated Gasification Combined Cycle) will be discussed as one of the most effective tools in CO<sub>2</sub> capture and consequently, in zero carbon power generation..

**Key words:** CO<sub>2</sub> capturing, sequestration, integrated gasification combined cycle

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Carbon capture from power generation can be accomplished by either of the following routes (Figure 1):

- Post-combustion capture
- Oxyfuel combustion
- Pre-combustion decarbonization
- Novel concepts

**Post-combustion CO<sub>2</sub> capture** is the most straight-forward technique. End-of-pipe treatment of the flue gases coming from conventional fossil-fired power plants belongs to this category. Its economical viability is poor because high volume of flue gas with relatively low CO<sub>2</sub> content has to be handled by conventional absorption process. This results in large equipment sizes and consequently high capital costs. Penalty in the loss of energy

generation is 25% - 35%. However, it can be suitable as retrofitting rebuilt of existing facilities, as for it does not virtually affect the upstream part of the original steam power plant.

**Oxyfuel combustion**, also called as oxyfuel decarbonization, or O<sub>2</sub>/CO<sub>2</sub> firing is more elegant. Instead of air, pure oxygen is used as the oxidant. Nitrogen is therefore eliminated from the process completely. Instead of nitrogen, CO<sub>2</sub> is recycled in a semi-closed cycle substituting thus the function of working fluid. For new installations it is more promising than the post-combustion process. The Air Separation Unit (ASU) is the biggest efficiency looser in this case. This loss, however, is compensated by the absence of any final CO<sub>2</sub> separation, because CO<sub>2</sub> is produced in a high sequestration-ready concentration, within the range 80 - 98%.

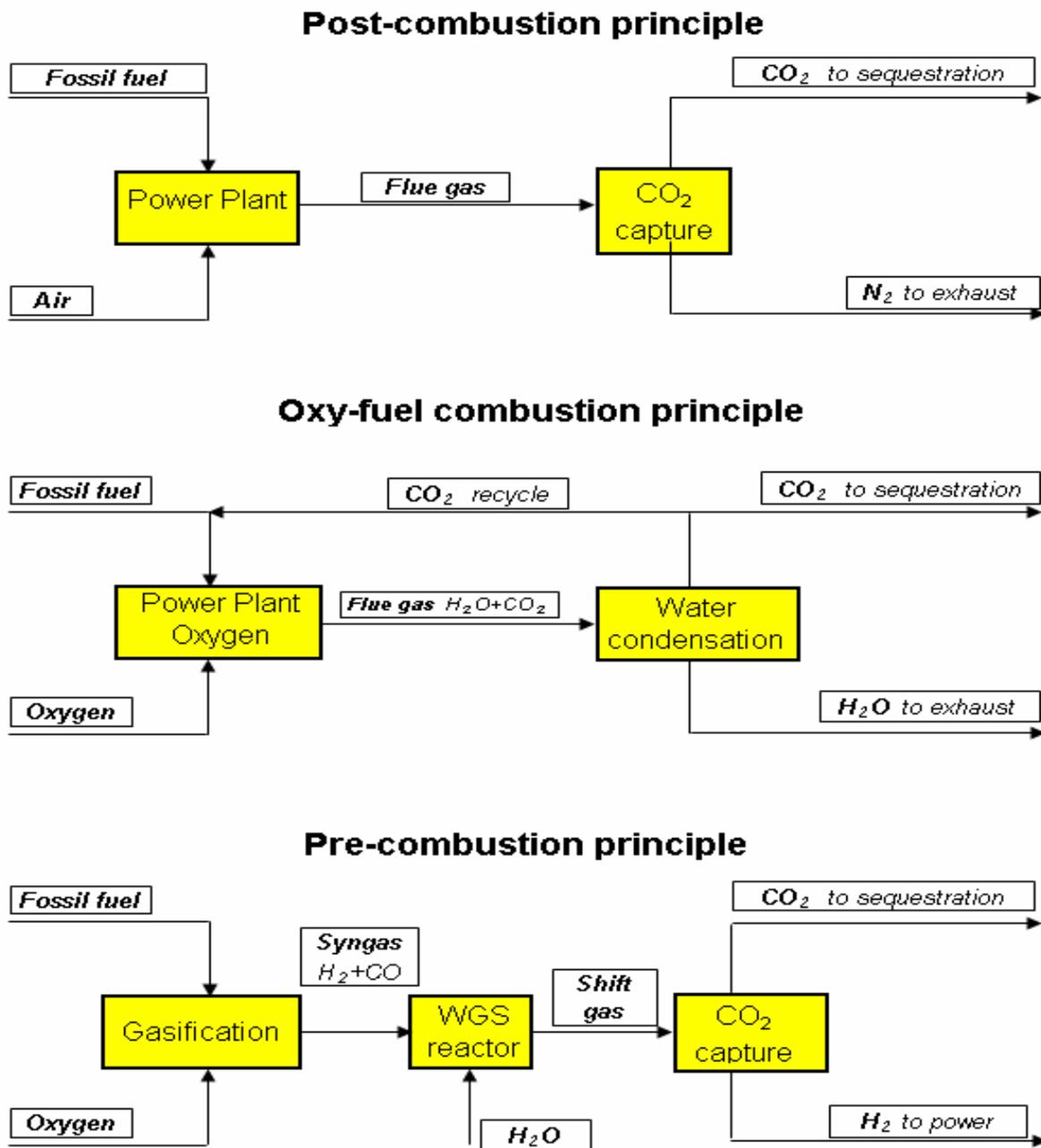


Figure 1: Options for power plant CO<sub>2</sub> capture for the sequestration purpose. WGS = Water Gas Shift process.

**Pre-combustion decarbonization** is exclusively based on the IGCC technology. In the first step, fossil fuel is transformed to synthesis gas (syngas), basically mixture of carbon monoxide (CO + H<sub>2</sub>). Syngas is then purified by one of the standard manners used with IGCC. In the next step CO is converted to H<sub>2</sub> + CO<sub>2</sub> via water-gas-shift (WGS) reaction. CO<sub>2</sub> is then separated by conventional methods. Its separation, however, consumes much less energy, because it takes place in a smaller reaction volume with lower volumetric flow rates, elevated pressure and higher component concentration. Higher concentrations make the capture process less energy intensive. Penalty in the loss of energy generation is typically 10-16% - half the one in a post-combustion decarbonization process. This technology is therefore *definitely* more effective than the postcombustion and *slightly* more effective than oxy-fuel decarbonization.

**Novel concepts** are based on techniques which are yet in the pilot-scale or even laboratory stage of development. Membrane processes of CO<sub>2</sub> separation or chemical looping are examples of these longer-term outlook technologies.

**Carbon sequestration.** General consent has been accepted that the current trend of CO<sub>2</sub> emissions is not acceptable. It should be reduced by several methods out of which carbon sequestration is generally supposed to play its important role in the future. By means of this technique CO<sub>2</sub> will be kept apart of the atmosphere by injecting it under surface. Its retention under the surface must be long enough (in order of centuries or one millennium) until the global atmospheric CO<sub>2</sub> equilibrium is re-established. This can be accomplished by either of the following methods.

**Carbon sequestration in geologic formations.**

This route has the following options.

- Storage in deep coal beds
- Storage in depleted oil and gas fields
- Storage in deep saline formations

**Carbon sequestration in deep sea** can be realized in various depths from 600m down to 3000 m and more.

**Environmental benefits of the carbon capture and sequestration**

**Anthropogenic carbon emissions** in the atmosphere are generally believed to be incrementally causing an imbalance in the global carbon cycle. Since the mid 19th century they have steadily grown by 2% annually up to the amount of 24 Gt/a CO<sub>2</sub> as of 2001. This is adequate to 6.5 Gt/a in *carbon equivalent*. More than half of this amount, 3.5 Gt/a, retains in the atmosphere while the balance is absorbed by the ocean and terrestrial biosphere. Cumulative amount of 260 Gt of carbon has been released from the burning of fossil fuels during the industrial period of the last 150 years.

**Global climate change.** The contribution of human-made CO<sub>2</sub> flux caused that the CO<sub>2</sub> concentration in the air has increased from 280 ppmv in 1850 to the current value of 360 ppmv. At the same time the global average temperature at the surface of the earth has increased by 0.8 °C.

Before this change occurred the temperature and CO<sub>2</sub> concentration profiles were swinging with almost regular amplitudes within the range of coordinates <180 ppmv, 280 ppmv> and <-8 °C, +3°C> respectively. Such course lasted throughout the history of the previous 420,000 years. Correlation between the temperature and carbon concentrations is evident.

**Stabilizing GHG concentrations** is by far more stringent target than stabilizing emissions. It may require that anthropogenic emissions must approach zero level unless legacy issues for future generations are left behind our generation.

Routes how to achieve such requirement are versatile. Their outline can have a following structure.

- Improved efficiency
  - Improved efficiency on the supply side
  - Improved efficiency on the demand side
- Fuel switching
  - Fuel switching towards higher H/C ratio (coal→oil, coal→gas, oil→gas)
  - Nuclear power

- Renewable energy
- Carbon capture and sequestration
  - Carbon sequestration in geologic formations
  - Carbon sequestration in the deep ocean

**Carbon capture and sequestration (CC&S)** is the most effective option as for it can be widely applied in the fossil fuel power generation which will be covering 80% of all energy production for a long time.

### Technological process of carbon capture

Many of the commercial technologies for CO<sub>2</sub> capture have seen applications as components of industrial processes. CO<sub>2</sub> capture technology is therefore available. However, it has only recently been seriously considered as a potential tool of reducing GHG emissions.

Review of possible CO<sub>2</sub> capture technologies is outlined below.

- Absorption processes
  - Chemical absorption with alkanolamine solvents, namely
    - family of primary amines like MEA (monoethanolamine) or DGA (diglycolamine)
    - family of secondary amines like DEA (diethanolamine) or DIPA (di-isopropanolamine)
    - family of tertiary amines like TEA (triethanolamine) or MDEA (methyldiethanolamine).
  - Physical absorption with solvents like
    - RECTISOL (cold methanol)
    - SELEXOL (dimethyl ether of polyethylene glycol)
    - Sulpholane (tetra-hydrothiophene dioxide)
    - Sulfinol (mixture of aqueous amine and sulfolane)

- Sulfinol-M (mixture of aqueous MDEA and Sulfolane)
- Fluor process (propylene carbonate)

- Adsorption processes
  - Adsorber beds
    - Alumina
    - Zeolite
    - Activated carbon
  - Regenerative adsorption processes
    - Pressure swing adsorption (PSA)
    - Temperature swing adsorption (TSA)
    - Electric swing adsorption (ESA)
    - Washing

- Cryogenic processes
- Membrane processes
  - Gas separation membranes
  - Polymeric membranes (micro porous)
    - Polypropylene
    - Polyphenyleneoxide
    - Polydimethylsiloxane
  - Porous inorganic membranes (zeolites)
  - Palladium membranes
- Microbial algal processes

Out of the above mentioned processes both chemical and physical **absorption** are mature and ready for CO<sub>2</sub> capture in bulk quantities to date. The only reason why they have not been used for CC&S purposes yet is the cost.

Results of research & development studies indicate that chemical absorption more suitable for postcombustion decarbonization while *physical* absorption fits better to precombustion decarbonization.

**Chemical solvents.** Alkanolamines are considered as best candidates for the postcombustion decarbonization of flue gases. They have been proven well as decarbonization solvents in the gas processing, chemical, and petroleum industries for more than half century. A typical flow diagram of such process is shown in Figure 2.

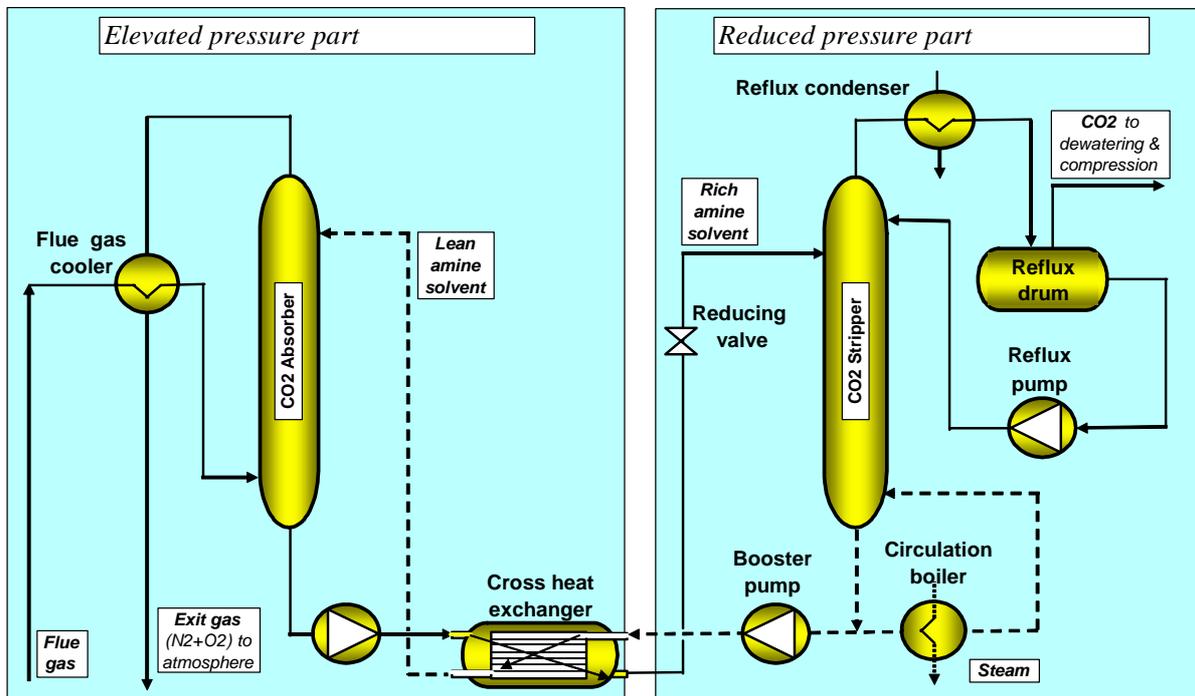


Figure 2: Process flow diagram of a general Flue Gas Decarbonization system

Upstream the absorption stage the CO<sub>2</sub> stream is first cooled and particulates are removed (only cooling stage is shown in Figure 2). In the next step it enters the absorption tower where it is contacted with the alkanolamine solvent in counter-current flow. The gas to be absorbed enters the absorber at its bottom, flows up, and leaves at its top. The solvent enters the top of the absorber, flows down, and emerges at the bottom. CO<sub>2</sub> is chemically bound with the solvent by the exothermic reaction of CO<sub>2</sub> with the amine functionality of the solvent. The liquid amine CO<sub>2</sub>-rich solvent leaves the bottom of the absorber, passes into the stripping tower via Cross Heat Exchanger. In the CO<sub>2</sub> Stripper, it is heated with steam to liberate the CO<sub>2</sub> off the solvent as the acid gas. This step is carried out at lower pressure than the previous absorption step to enhance desorption of CO<sub>2</sub> from the liquid. CO<sub>2</sub> is then ready for further steps of compression, transport from power plant to a storage site and its long term storage (aquifers, depleted oil/gas etc.)

The hot lean amine solution then flows through the Cross Heat Exchanger where it is contacted with the rich amine solution from the Absorber. The lean amine solution from the Cross Heat

Exchanger is returned to the top of the Absorption tower. Absorption with Amines have been practiced in large scale in the natural gas processing industry to remove H<sub>2</sub>S and CO<sub>2</sub> from natural gas. Their direct adoption to flue gas decarbonization has two problems. First, CO<sub>2</sub> occurs in the flue gas in bulk quantity, while in natural gas only as an impurity. Second, decarbonization of natural gas must address the presence of hydrogen sulfide (H<sub>2</sub>S) while there is no H<sub>2</sub>S in flue gases.

The greatest issue in postcombustion decarbonization is the low pressure (atmospheric) of the flue gas. Only chemical solvents with high reaction energies like alkanolamines can economically scrub CO<sub>2</sub> under such low partial pressures.

There is considerable industrial experience with **primary amines** chemical absorption solvents, especially with MEA. It is one of the most frequently used solvents for CO<sub>2</sub> capture. It is the cheapest and its capture reaction heat 1.9 MJ/kg is the highest. Its molecular weight is the lowest, therefore it has the highest theoretical absorption capacity but also the lowest boiling

point. The latter property may cause solvent carryover in the carbon dioxide removal from the gas stream and also in the regeneration step. Another drawback is the high reactivity with COS and CS<sub>2</sub> resulting in solvent degradation. Also the CO<sub>2</sub> causes high corrosivity, because CO<sub>2</sub> itself is a strong corrosivity agent. The process has been used to treat flue gas. Its energy consumption is significant for flue gas treatment.

**Secondary amines** have lower capture reaction heat. E.g. reaction heat of DEA is 1.5 MJ/kg. It is therefore more economical in the regeneration step than MEA.

**Tertiary amines** are even less reactive, with lowest heat requirements for carbon dioxide liberation from the carbon dioxide containing solvent (MDEA – 1.3 MJ/kg). However, higher circulation rate of solvent is necessary. Tertiary amines are less sensitive to degradation processes and have also lower corrosion rates than primary and secondary amines.

### Precombustion carbon capture

Technology of precombustion capture of CO<sub>2</sub> via gasification already exists as a well established industrial process. It is known as a technological segment of hydrogen production processes commonly used and proven in ammonia production, oil refinery or methanol synthesis. The water gas shift stage is usually in the centre of the process. Double benefit of production of valuable hydrogen in parallel with CO<sub>2</sub> separation step means added commercial value. Another advantage of hydrogen coproduction is the possibility of fuel cells integration for power generation purposes, but also for transportation (in the medium-term outlook, hydrogen is supposed to become the transportation fuel of choice).

A general simplified flow diagram of an IGCC system integrated with carbon capture based on a heavy feedstock is shown in Figure 3.

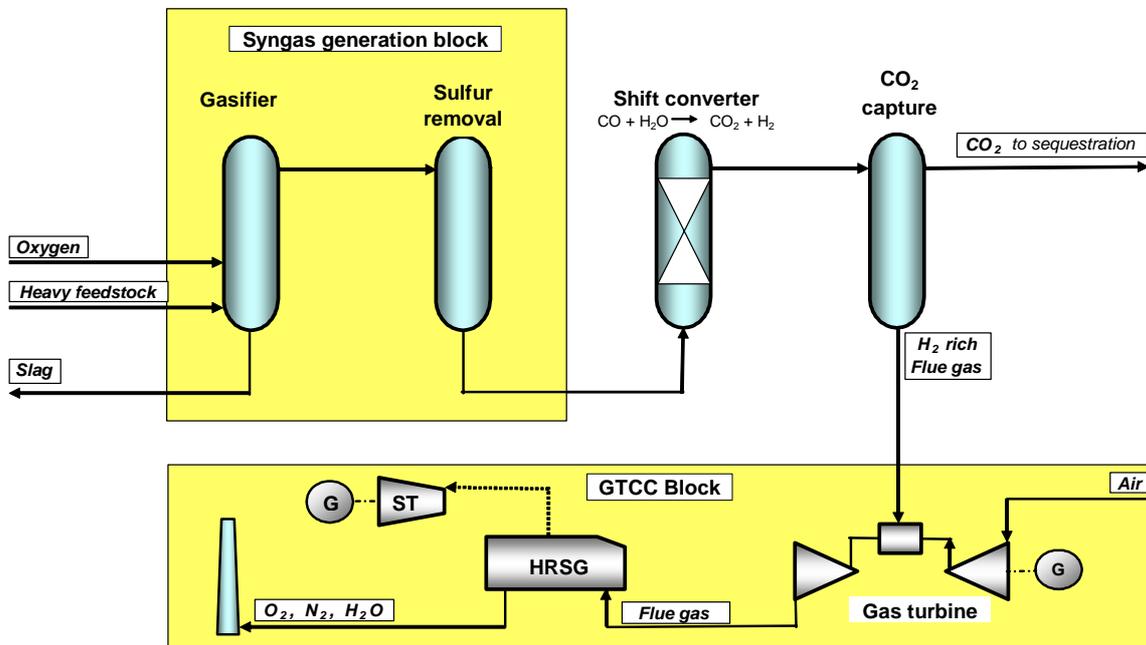


Figure 3: Simplified flow diagram of IGCC system based on a heavy feedstock (coal, petcoke, petroleum residue etc.) and equipped with pre-combustion capture of CO<sub>2</sub>

The formula of technological sequence

*Syngas generation block* → *Water gas shift reactor* → *CO<sub>2</sub> capture* → *GTCC*

is typical, yet not inevitable. Modifications to this standard may occur in the sequence of refinery steps.

A similar flow diagram of an IGCC system integrated with carbon capture based on natural gas feedstock is shown in Figure 4.

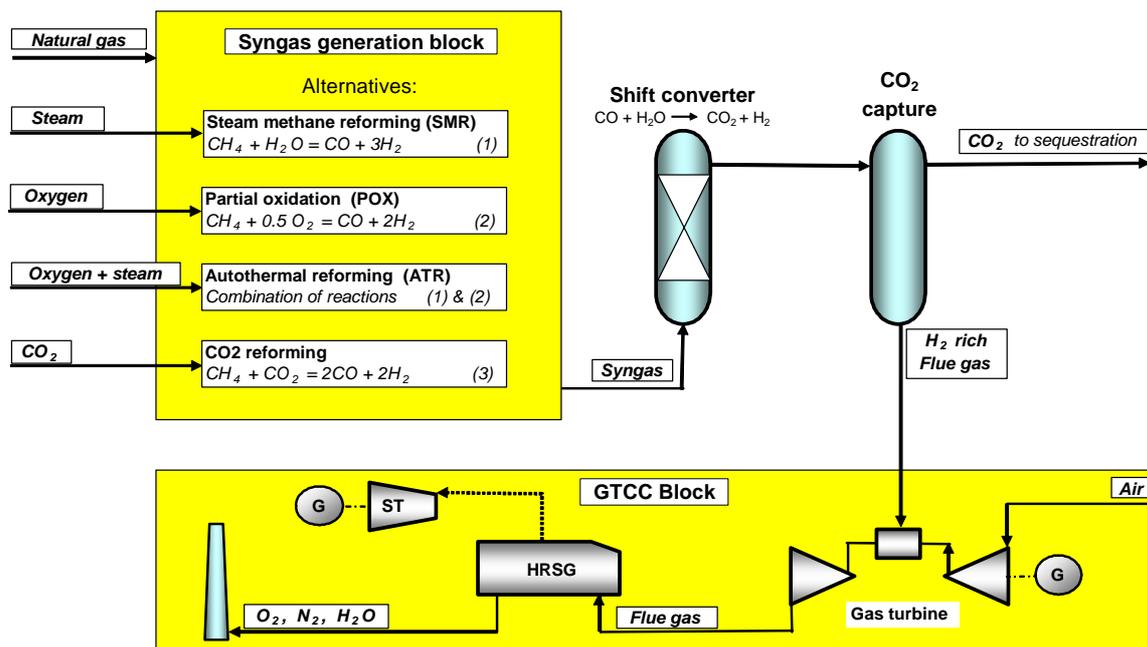


Figure 4: Simplified flow diagram of IGCC system based on a natural gas equipped with pre-combustion capture of CO<sub>2</sub>

The difference between both schemes is in the utility sense of the IGCC concept itself. In the case of heavy fuel feedstock application of the IGCC concept is inevitable whether the sequestration stage follows after it or not. This is because heavy fuel cannot be burned in a gas turbine. On the other hand, IGCC concept in the case of natural gas feedstock would not be justified without the existence of a downstream sequestration stage. Conventional GTCC (Gas Turbine Combined Cycle) would be preferable instead.

The fact that in both cases the gas turbine is fired with hydrogen rich fuel deserves attention. Commercial gas turbines are normally designed for natural gas or oil operation. Their

compatibility to hydrogen operation needs certain redesign, though not substantial.

When using natural gas as feedstock, syngas is produced by either of technologies outlined in Figure 4. The CO is reacted with steam in a catalytic process of the WGS reaction to produce CO<sub>2</sub> and highest possible amount of H<sub>2</sub>. After the CO-conversion and removal of condensate, the gas mainly consists of H<sub>2</sub> with CO<sub>2</sub>. The CO<sub>2</sub> can then be separated by chemical or physical absorption for disposal or use. The H<sub>2</sub> can be used as a chemical feedstock, or as fuel in a GTCC plant or eventually a fuel cell. Chemical or physical gas absorption equipped with a stripping regeneration stage, generally called as the Cold Gas Cleanup – CGU has been used almost

exclusively for the syngas desulphurization in all of the IGCC projects realized (except for Pinon Pine Sierra Pacific) up to date. What was good for desulphurization will be good for decarbonisation as well, even though with appropriate modifications. At least such are conclusions of majority of research & development studies on this subject.

Elevated pressure and relatively high concentration of CO<sub>2</sub> in the synthesis gas are cost-reducing factors. Comparison with other competitive carbon sources as possible candidates to carbon capture are reviewed below as typical values.

Coal fired boiler flue gas	14%
Natural gas fired boiler flue gas	8%
Natural gas combined cycle flue gas	4%
Natural gas partial oxidation fuel gas	24%
Oxy-fuel combustion flue gas >	80%
Coal gasification synthesis gas	40%

The low concentration of CO<sub>2</sub> in conventional combustion means that a large volume of gas has to be handled, resulting in large equipment sizes. Moreover, strong-affinity chemical solvents have to be used to capture such small concentrations of CO<sub>2</sub> in such a big volume.

Absorption of CO<sub>2</sub> in MDEA solvent is very efficient and strong. Unfortunately, the stronger is capture the more heat consumption must be expended to its release in the regeneration stage. Apart from this disadvantage a strong chemical degradation sensitivity to SO<sub>2</sub> and NO<sub>2</sub> exists. In the presence of oxygen also their corrosion aggression is considerable.

Despite all drawbacks current commercial use of alkanolamine MDEA is high with IGCC. Projects like Plaquemine 1986, Wabash River 1995, Tampa Electric 1996, Puertollano 1997, ISAB Energy 2000, Motiva Delaware 2000, and Piensa 2006 employ MDEA process. Reason for such massive deployment is that MDEA is highly effective with desulphurization of syngas. Of course, this does not mean that the same competitiveness of MDEA will be reproduced in the future applications of the desulphurization → CO<sub>2</sub> capture → CO<sub>2</sub> sequestration process. On contrary, preliminary experience confirms that physical solvents may be more effective for this purpose, as discussed below.

### Physical solvents.

If the CO<sub>2</sub> concentration and pressure could be increased, the CO<sub>2</sub> capture equipment would be

smaller and physical solvents could be used, with lower energy penalties for regeneration. Exactly this is the case for CO<sub>2</sub> separation in pre-combustion capture processes applied to IGCC. Compare to combustion flue gases, in this case CO<sub>2</sub> concentration is 3 times higher while pressure upstream the gas turbine is typically 20 times higher. Volume concentration of the CO<sub>2</sub> is therefore 60 times higher compare to a typical coal flue gas. The advantage in this case is a lower heat consumption in the solvent regeneration step, when no additional heat is necessary and the stripping is driven mainly by the pressure release (flash distillation).

**RECTISOL** process is one of the most effective procedures for precombustion CO<sub>2</sub> capture from a IGCC plant based on heavy fuel gasification. RECTISOL process with intermediate water-gas-shift offers multiple benefit, like

- desulphurization,
- additional hydrogen generation via WGS,
- hydrogen separation, and
- CO<sub>2</sub> capture,

all in a single integrated train. Such configuration has been applied in the SGP IGCC project Pernis (127 MWe) as its first-of-a-kind IGCC application equipped with CO<sub>2</sub> separation. The only exclusion is that no CO<sub>2</sub> capture has been realized in this case while the separated CO<sub>2</sub> is vented as the tail-gas. With this arrangement plant Pernis has qualified itself as being the first and so far the only *sequestration-ready* true IGCC plant. Single-circuit RECTISOL process has been applied to the IGCC projects SU a.s. Vresova 350 MWe, Czech Republic and Global Energy Inc. Schwarze Pumpe, Germany (most IGCC operators prefer MDEA for desulphurization).

**SELEXOL** is another physical solvent competitive to RECTISOL. There are 55 SELEXOL operating units in syngas and natural gas service. In relation to the desulphurization in IGCC, SELEXOL has less instances than RECTISOL. On the other hand, as far as hydrogen production or CO<sub>2</sub> capture is the priority, SELEXOL moderately outperforms RECTISOL. List of references of this kind comprises several important refinery IGCC projects as indicated in Table 1.

**Table 1 Review of SELEXOL applications in gasification projects**

Plant Owner	Country	Start-up	Feedstock	Gasification process	Application
SCE Cool Water	USA	1984	bituminous coal	Texaco	IGCC
Farmland Industries, Inc.	USA	2000	pet coke	Texaco	Ammonia
API Energia S.P.A.	Italy	2001	visbreaker res.	Texaco	IGCC, H <sub>2</sub>
SARLUX srl	Italy	2001	visbreaker res.	Texaco	IGCC
Total Fina Elf/Texaco	France	2006	refinery res.	Texaco	H <sub>2</sub>
Mitteldeutsche Erdöl Raff.	Ger.	1985	visbreak.res.	Shell	Methanol

Out of the six projects listed in Table 1 item entitled *Farmland Industries, Inc. Gasification - petcoke to ammonia* is also one which meets criterion of a CO<sub>2</sub> ready-to-sequestration plant. Process flow diagram of its SELEXOL cleanup unit is shown in Figure 5.

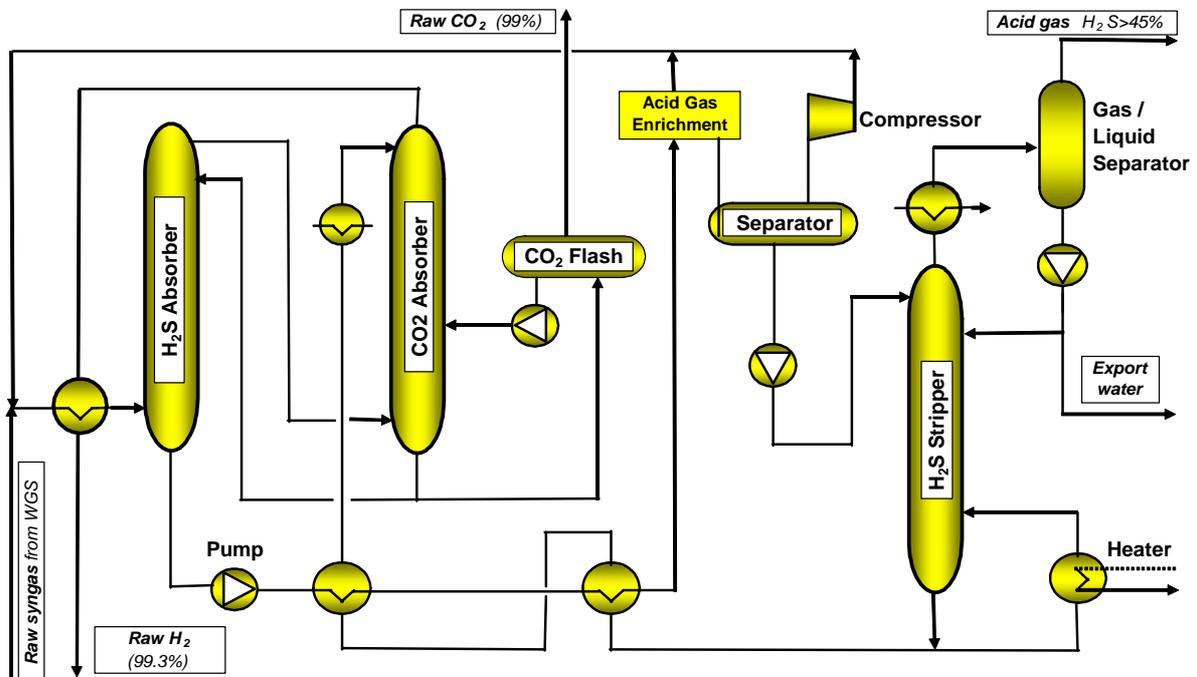


Figure 5: Flow diagram of the SELEXOL process of the Farmland ammonia plant. Syngas feed composition is 50% H<sub>2</sub>, 40% CO<sub>2</sub>

The process is configured from two refining circuits. Triple effect of hydrogen production, desulphurization and CO<sub>2</sub> separation respectively, can be won in this way. Acid gas leaves the H<sub>2</sub>S Stripper circuit with concentration H<sub>2</sub>S > 45%, well enough to meet requirements of the downstream Claus process. Raw CO<sub>2</sub> leaving the CO<sub>2</sub> Flash Tank is removed also in a state with ready-to-sequestration purity of 99%.

The raw hydrogen has purity 99.3% (its final purification is performed in a downstream POLYBEDTM PSA unit).

It should be pointed out that the same as Farmland ammonia plant any ammonia technology can be formally construed as carbon ready-to-sequestration technology. Such are for example all plants producing ammonia or

methanol reviewed in Table 4-1. Such are also any other plants producing CO<sub>2</sub> as intermediate product or by-product in isolated form. The key is hydrogen. Wherever hydrogen is generated via water-gas-shift reaction CO<sub>2</sub> is usually co produced in considerable concentration. Unless it is used as further processing feedstock it offers potential to being sequestered.

### Oxyfuel combustion

Oxidant is used in its concentrated form i.e. in the form of pure oxygen in oxyfuel combustion. Its advantage consists in the elimination of the CO<sub>2</sub> separation step. Instead, only water has to be removed from the flue gas by simple condensation.

The basic approach of oxyfuel combustion was introduced in Figure 1. The biggest energy

consumption is in the stage of oxygen generation. A broad research & development effort is in progress worldwide to reduce these costs. Most advanced processes are based on membrane technology operating at high temperatures. Overall plant efficiency and economics can be improved in this way, confirmed by the results demonstrated on small scale test rigs. Large scale applications have been carried out in glass and steel melting furnaces. Retrofit transformation of existing steam power plants is possible and does not mean too big additional costs.

Basic concept of oxyfuel combustion incorporated in the combined cycle is shown in Figure 6.

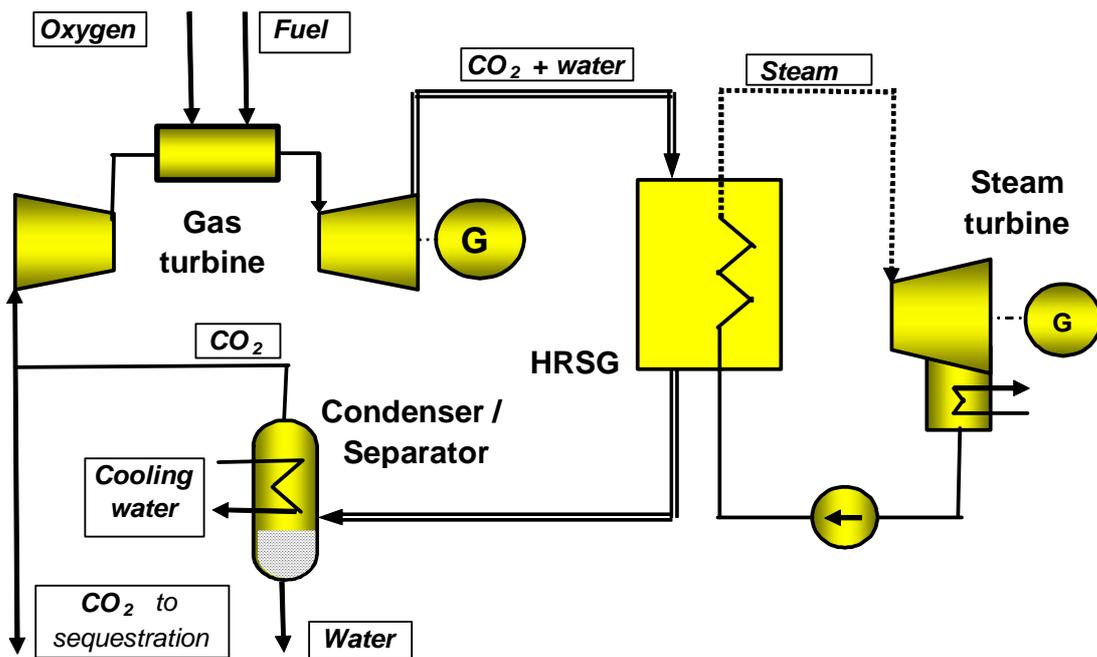


Figure 6: Outline of the oxyfuel combined cycle system working in a semi - closed cycle with CO<sub>2</sub> recirculation. Standard GTCC arrangement with Heat Recovery Steam Generator (HRSG) and condensing steam turbine is used.

The key elements of this process are

- Air separation unit (not indicated in Figure 6) generating pure oxygen. Gas turbine specially designed for operation with  $\text{CO}_2 / \text{H}_2\text{O}$  working fluid. Control system precisely watching the stoichiometric ratio between the streams of fuel and oxygen being injected in the combustion chamber, to prevent that either unreacted fuel or oxygen occurs downstream the combustion chamber.
- Rankine cycle circuit (HRSG, steam turbine with condenser as well as other equipment not indicated in Figure 6).
- Condenser / Separator in which carbon dioxide is separated from water. Compressor / pumping / heat exchanger system necessary to pump the carbon dioxide into an injection well.

If natural gas is used as the fuel this concept represents another alternative to pre-combustion

capture system shown in Figure 4. Problem in this case is only that gas turbines using  $\text{CO}_2$  as the operating fluid impose bigger challenge than hydrogen-rich fuel fired gas turbines. Retrofit projects of this kind would not be feasible at all as for the re-design of existing gas turbines would not come to consideration. Greenfield projects of this kind are possible in the future but certain development activities have to be expended.

Another alternative for gas turbine oxyfuel principle is one in which water steam instead of  $\text{CO}_2$  is used as the operating fluid. Such concept is shown in Figure 7.

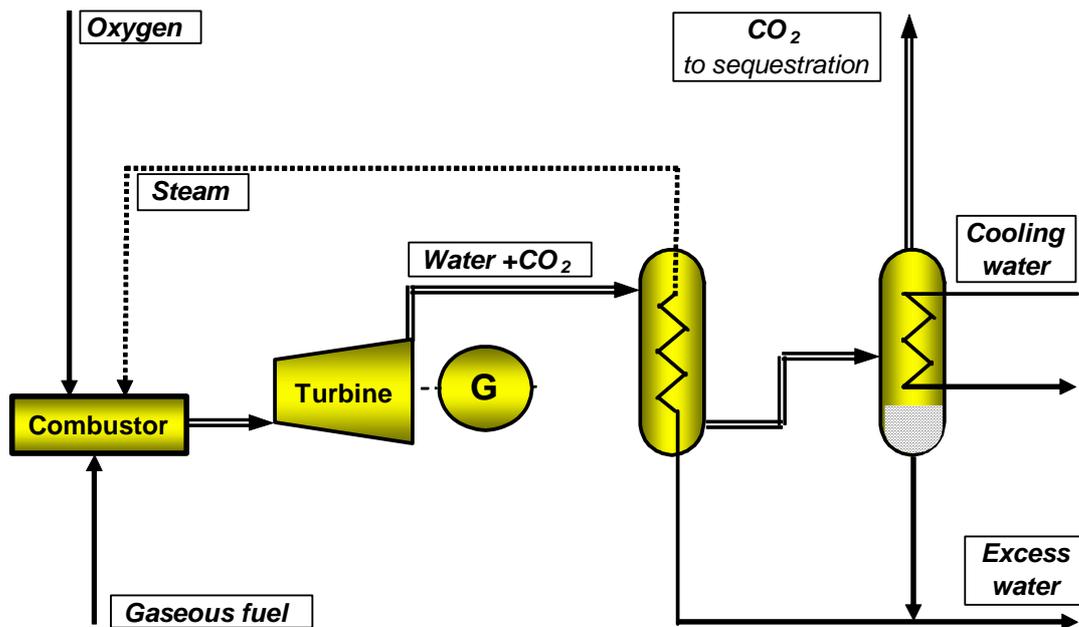


Figure 7: Process layout of the steam-water oxyfuel combustion system. Fuel can be natural gas, syngas or similar. Prime mover is quasi steam turbine whose working fluid is a mixture of water steam +  $\text{CO}_2$  with steam content prevailing. Metering of oxygen and gaseous fuel must be adjusted in the stoichiometric ratio.

## Novel concepts of carbon capture & sequestration

„Novel concepts of carbon capture and sequestration“ is the term under which we understand technologies whose commercial realization by means of state-of-the-art technical means is not possible yet. Their bench-scale or pilot plant-scale development is currently underway.

The following technologies of this kind serve as examples.

- CO<sub>2</sub> capture by means of the ion transport membranes
- Chemical looping process
- CO<sub>2</sub> hydrate process

**Ion Transport Membranes (ITM)** are devices able to transport oxygen ions selectively. In this way oxygen separation from its mixture with other gases is made possible. Such process is by far more economical than the state-of-the-art cryogenic process which is highly energy intensive. The media effective are ceramic, non-porous, mixed-conducting membranes operating by virtue of transport selectivity upon oxygen ions. The membrane substance is composed of conductors made of mixed-metal oxides. Their conductivity state is initialized at high excitation temperatures, typically 800°C to 900°C. At these temperatures the ITMs exhibit both electric and oxygen ion conductivity. They are stoichiometrically oxygen deficient, which causes creation of oxygen vacancies in their crystal lattice.

The ion transport mechanism is based on the principle of ionic exclusion. Oxygen from the air adsorbs on the surface of the membrane. Then it dissociates and ionizes and releases electrons from the membrane. The oxygen anions occupy vacancies in the lattice and diffuse through the membrane, driven by an oxygen chemical-potential gradient. This gradient is proportional to the difference between the respective oxygen partial pressures on opposite sides of the membrane. At the permeate surface of the membrane, the oxygen ions release their electrons. Subsequently they recombine, and

desorbs from the surface as neutral oxygen molecules. No affinity exists for transport of other ions. Consequently, the separation selectivity for oxygen is absolute. The primary purpose of ITMs is the air decomposition to oxygen and nitrogen. The economical benefit following from their possible commercial success would be immense if we take to consideration the enormous energy intensity of the currently used cryogenic processes.

Secondary purpose for their application is the possibility of an indirect CO<sub>2</sub> capture. Such opportunity is created by virtue of the gas turbine combustion chamber. In the first step direct separation of oxygen from the air is carried out. Subsequently, fuel combustion takes place at the opposite (permeate) side of the membrane. Virtually, this arrangement operates like a combustor with inherent capability of CO<sub>2</sub> separation.

Combination of gas turbine with the ITM reactor is a witty idea from the point of physical sense. The flow rate of oxygen across the membrane surface is proportional to the difference of concentrations (partial pressures) of oxygen on both sides. The lower is the concentration on the permeate side the better is the whole process driven. Advantage is that oxygen on the permeate side is permanently withdrawn as the consequence of combustion. This is not the case in standard arrangement of the ITM at which oxygen is produced as the product.

The idea of integration of ITM with gas turbine was originally proposed by Norsk Hydro. It has been further developed by Alstom who is now involved in an EU-sponsored project called AZEP (Advanced Zero Emission Power Plant).

Success in the introduction of ITM may come relatively soon (several years), being fuelled by a strong commercial incentive. The currently used cryogenic technology is heavily energy intensive and at the same time it impacts several industries at once, like steel production, glass production, petrochemistry, chemical synthesis etc.

### CO<sub>2</sub> capture by means of Chemical Looping

Chemical Looping process makes possible to execute both fuel combustion and CO<sub>2</sub> separation in one gemini equipment. The process itself, is a closed-circuit ion transfer, as shown in Figure 8.

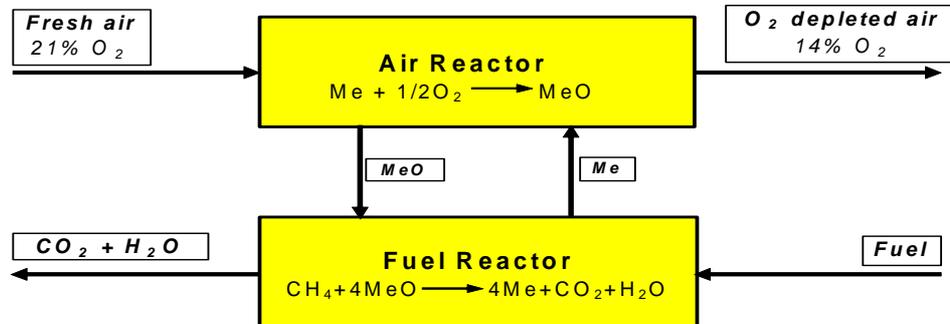


Figure 8: Basic principle of the Chemical Looping Process

The metal oxide transfers oxygen from the combustion air to the fuel. Similarly as was the case with ITM system also in this case the direct contact between fuel and combustion air is avoided. This is made possible by virtue of two fluid reactors operating as oxygen exchangers as outlined in Figure 9.

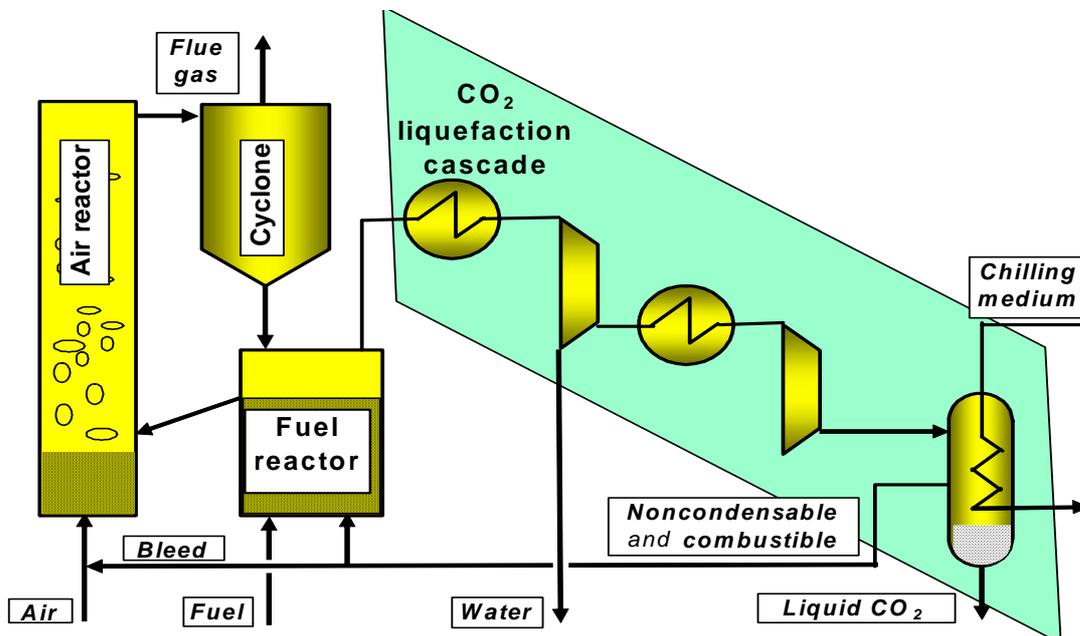


Figure 9: Process flow diagram of the chemical-looping system using two interconnected fluid reactors exchanging oxygen between two forms of the metaloxide carrier.

Both reactors have interconnected their fluidized beds as follows.

- In the Fuel Reactor the metal oxide is reduced by reaction with the fuel. Its outlet gas consists of CO<sub>2</sub> + H<sub>2</sub>O.
- In the Air Reactor the reduced metal oxide is oxidized with air. Its outlet gas consists of nitrogen plus reduced amount of oxygen.

The net summary chemical reaction over the two reactors is the same as for normal combustion with the same amount of heat released. The

process could be therefore called *pseudocombustion* as well. Its advantage is that CO<sub>2</sub> is inherently separated off and no extra energy is to be expended for this purpose.

### CO<sub>2</sub> hydrate process

CO<sub>2</sub> hydrate process is another example from the portfolio of CO<sub>2</sub> capture processes specifically suitable for IGCC technology comprising the water-gas-shift reactor. Its conceptual flow diagram is shown in Figure 10.

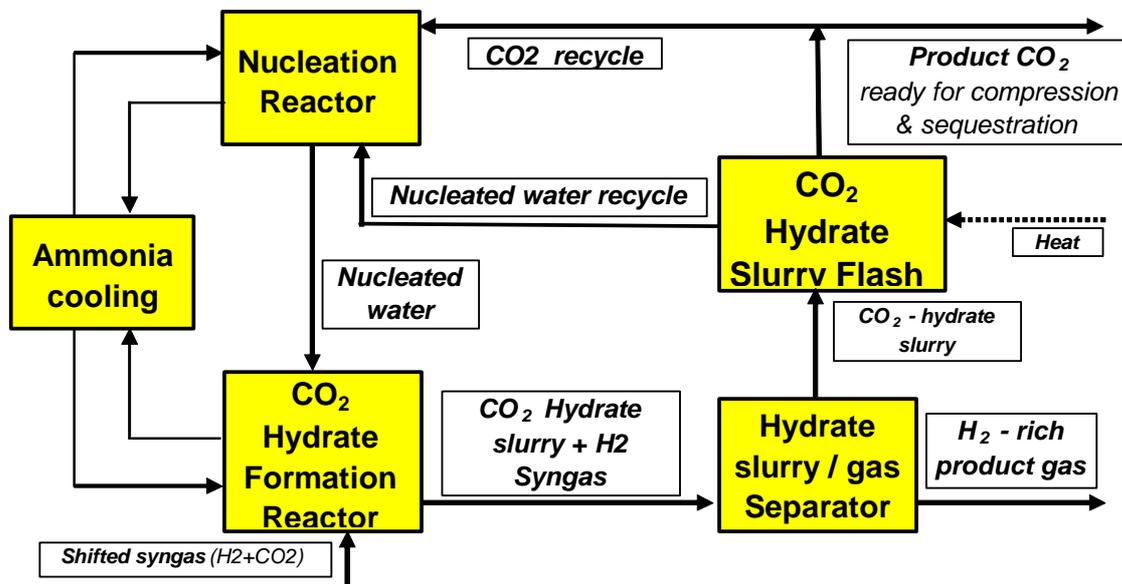


Figure 10: Simplified flow diagram of a CO<sub>2</sub> Hydrate Process. Process parameters: 1 - 3°C, 30 - 55 bar

The process is based on the absorption ability of water to create hydrates with CO<sub>2</sub> at high pressure and very low temperature. This requires ammonia refrigeration. CO<sub>2</sub> is hydrated in the CO<sub>2</sub> Hydrate Formation Reactor with nucleated water coming from the Nucleation Reactor. Nucleation process consist in creation of enough active centres called *nuclei* in a solvent, water in this case. In the further step

the nuclei promote massive hydration of CO<sub>2</sub> to give rise to hydrate slurry. In the next step CO<sub>2</sub> can be separated from its hydrate slurry on mild conditions.

The process promises good results in the economy of CO<sub>2</sub> capture with low penalty in the efficiency and low capital and operating costs.

**CO<sub>2</sub> sequestration opportunities**  
**Carbon sequestration in geologic formations.**

This route has the following options and potential storage capacities (in order).

- Storage in deep coal beds - capacity 10 – 1000 Gt
- Storage in depleted oil and gas fields - capacity 100 – 1000+ Gt
- Storage in deep saline formations - capacity 100 – 10,000 Gt

(1 Gt = 10<sup>9</sup> metric tons).

CO<sub>2</sub> storage in deep coal beds may be a promising pathway with agreeable kind of “geological sink” for storing CO<sub>2</sub> emissions in unmineable coal beds. At the same time the production of natural gas (CH<sub>4</sub>) from gassy coal beds can be significantly increased. Outline of the arrangement and function of the CO<sub>2</sub> sequestration process in coal beds is given in Figure 11.

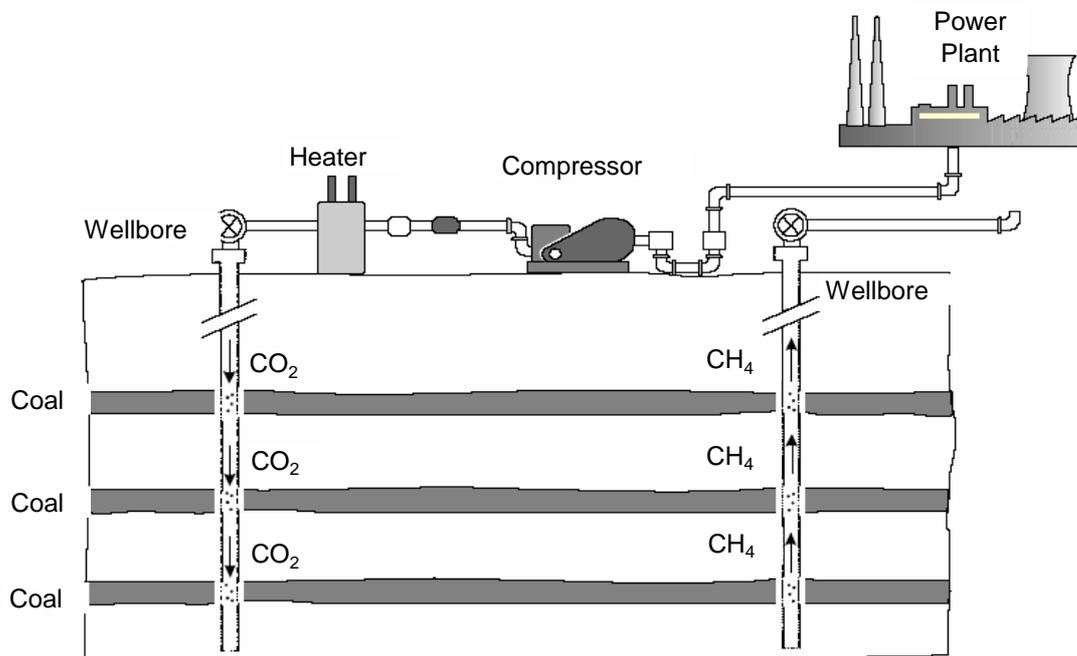


Figure 11: Outline of the arrangement and function of the CO<sub>2</sub> sequestration process in coal beds.  
 Courtesy of the US DOE - NETL (National Energy Technology Laboratory)

CO<sub>2</sub> storage in depleted oil and gas fields has a similar arrangement of CO<sub>2</sub> injection by the inlet pipe and oil or gas extraction by the outlet pipe.

Storage in deep saline formations does not provide any additional effect of enhanced extraction of minerals. Nevertheless its potential capacity for CO<sub>2</sub> sequestration is the biggest.

**Carbon sequestration in deep sea** can be realized in various depths from 600m down to

3000 m and more. In general, the deeper is the storage the more costly is the sequestration process but the safer and less harmful to the environment it is. Storage capacity of oceans is huge, in order of 1,000 – 10,000+ Gt.

**Conclusions**

Carbon capture and sequestration is the most effective option to solve green house gas issue in the future. Reason for this is that it can be widely applied in the fossil fuel power generation

which will be covering 80% of all energy production for a long time.

The other competitive technologies are restricted in their application either by their prohibitive price (solar, wind, hydro) and/or by lower carbon reducing efficiency.

Negligible contribution is expected from nuclear power generation. The current trend of declining nuclear power continues worldwide. Public concerns about plant safety, radioactive waste disposal, and weapons proliferation are expected to continue.

In summary – efficiency improvements, switch to low carbon fuels and renewable are good for

mankind. They are very useful and necessary, yet not sufficient to mitigate the global warming problem. “Clean fossil” generation equipped with CC&S as the supplement to these standard tools appears to become inevitable.

However conservative the above considerations may seem, the message is clear. World’s power generation reliance on fossil fuels will retain its dominance for the foreseeable future, whether we like it or not. In the light of the tremendous challenge of near zero target in carbon emissions this appears impossible without massive implementation of the CC&S technologies in the future.

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