ZERO CARBON POWER GENERATION: IGCC AS THE PREMIUM OPTION

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INTRODUCTION

The idea of capturing **C**arbon **D**ioxide (CO_2) from flue gases is not new. Historically, its origins were not related to **G**reen **H**ouse **G**ases (GHG).

First commercial applications were realized in the field of Enhanced Oil Recovery (USA, 1977 – 1984). CO_2 has been injected in the oil reservoirs to increase the mobility of oil.

It was not before 1996, when the first commercial CO_2 capture with sequestration motivated by GHG reduction was realized.

In 1996 Statoil of Norway began injecting CO_2 beneath the bottom of the North Sea. The stiff Norwegian carbon tax was the strong incentive in this pioneering project.

In this Article the role of gasification and specifically the role of **I**ntegrated **G**asification **C**ombined **C**ycle (IGCC) will be discussed as one of the most effective tools in CO_2 capture and consequently, in zero carbon power generation.

Carbon capture from power generation can be accomplished by either of the following routes:

- ➢ Post-combustion capture
- ➢ Oxy-fuel combustion
- ➢ Pre-combustion de-carbonization
- ➢ Novel concepts

CO_2 EMISSIONS FROM POWER GENERATION

During last 160 years the atmospheric levels of CO_2 have risen from around 280 parts per million (ppmv) to present levels of 360 ppmv.

This rise in atmospheric CO_2 levels is due primarily to expanding use of fossil fuels for electrical power generation.

Predictions of global energy use in the next century suggest a continued increase in carbon emissions and rising concentrations of CO_2 in the atmosphere unless major changes are made in the way we produce and use energy as well as "how we manage carbon.

The current state-of-art of conventional supercritical (SC) and/or ultra-supercritical (USC) **P**ulverized **C**oal (PC) power generation technology with **F**lue **G**as **D**esulphurization (FGD) systems are working with efficiency in the range of 40-46%.

To open up further efficiency potentials, the electricity supply industries are developing even more advanced power plant concepts using advanced materials for boiler and **S**team **T**urbine (ST).

It will thus be possible in the future to step up the efficiency by 4 to 5%. Beyond 2010, these power plant concepts would allow net efficiency potentials of 48 to 50%.

The development of new alloys for boiler and ST can push the efficiency to 50-52% in 2020 and further development could offer 52-55% in 2050.

The following thermal power plant efficiencies were considered for evaluation in this paragraph:

- CCGT (NG) System $\rightarrow$ 54%
- CCGT (Oil) System $\rightarrow$ 48%
- IGCC System $\rightarrow$ 43%
- PC / FGD System $\rightarrow$ 41%
- PFBC System $\rightarrow$ 40%
- CO_2 Recycle System $\rightarrow$ 34%

Estimated efficiency of the CO_2 recycle scheme is rather low but it could still be competitive with alternative schemes once the cost for CO_2 capture is included. The assumed efficiencies ranges are dependent on various other assumptions such as the art of technology, extent of heat recovery economics at the assumed capital charge and predictions, fuel quality and plant operation mode (based on continuous maximum load mode).

It seems reasonable to assume that the efficiency predictions for the PF+FGD and GTCC cases are fairly accurate. Even that the IGCC is more developed than CO_2 recycle, but is still not considered as fully established commercial technology. It may be stated that in the absence of any recovery, the amount of CO_2 released for a given fuel is inversely proportional to the process efficiency.

Table 1 illustrates the range of CO_2 emissions for each of the base cases examined. As can be seen, the natural gas fired option produces significantly less CO_2 per unit of power generated, than the coal fired options and is not very sensitive to the assumptions made.

POS	POWER GENERATION SYSTEM	CO_2 EMISSIONS TON / MWH
1	CCGT (NG) System	0.35 – 0.40
2	CCGT (Oil) System	0.45 – 0.55
3	IGCC System	0.60 - 0.80
4	PC / FGD System	0.70 – 1.00
5	PFBC System	0.75 – 1.05
6	CO_2 Recycle System	0.90 – 1.20

TABLE 1
RANGE OF CO_2 EMISSIONS FOR VARIOUS POWER GENERATION SYSTEMS

The coal fired options show a considerable range of CO_2 emissions as a result of significant variations in the efficiency of power generation.

The results illustrate the often suggested 'fuel substitution' argument; that use of a fuel with a low carbon to hydrogen ratio, significantly reduces the emissions of CO_2.

CO_2 emissions from oil fired power plants are depending on the oil quality (e.g. how heavy the oil is).

Coal based Pressurized Fluidized Bed Combustion (PFBC) technique would have similar CO_2 emissions to the IGCC and CF options.

CARBON CAPTURE FROM POWER GENERATION

Post-combustion CO_2 Capture is the most straight-forward technique. End-of-pipe treatment of flue gases produced conventional, fossil-fired, power plants belongs to this category.

Economical viability of technique is rather poor due to very high flue gas volume with relatively low CO_2 content which has to be handled by conventional absorption process, resulting in large equipment sizes and consequently very high capital costs.

Additionally, the power generation plant is penalized by means of power generation loss in the level of 25% - 35%. However, this technique is very well suitable for retrofitting of existing facilities, as for it does not virtually affect the upstream part of the original power generation plant.

Oxy-fuel Combustion (Figure 1), also called as oxy-fuel de-carbonization, or O_2/CO_2 firing is more elegant technique. Instead of air, pure oxygen is used as the oxidant.

Nitrogen is completely eliminated from the process. Instead of nitrogen, CO_2 is recycled in a semi-closed cycle substituting thus the function of working fluid.

This technique is much more promising for new installations 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_2 separation, because CO_2 is produced in a high sequestration-ready concentration, within the range 80 - 98%.
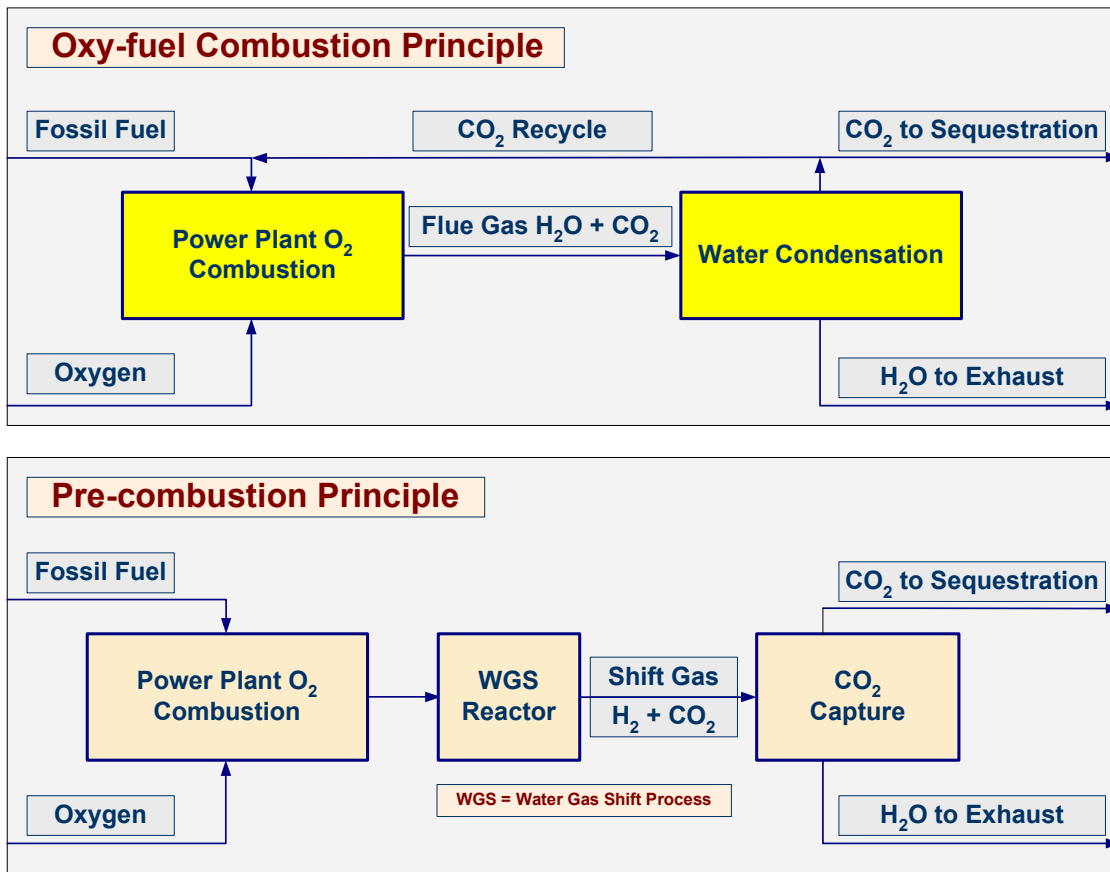
FIGURE 1

OPTIONS FOR POWER PLANT CO_2 CAPTURE FOR THE SEQUESTRATION PURPOSE

Pre-combustion De-carbonization (Figure 1) 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) + hydrogen (H_2).

Syngas is then purified by one of the standard manners used with IGCC. In the next step CO is converted to H_2 + CO_2 via **W**ater-**G**as-**S**hift (WGS) reaction.

CO_2 is then separated by conventional methods. The CO_2 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% which is roughly half of the post-combustion de-carbonization processes.

This technology is therefore *definitely* more effective than the post-combustion and *slightly* more effective than oxy-fuel de-carbonization.

Novel Concepts are based on techniques which are yet in the pilot-scale or even laboratory stage of development. Membrane processes of CO_2 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_2 emissions is not acceptable. CO_2 emissions must be reduced by either method, but the carbon sequestration is expected to play most important role in the future. By means of this technique CO_2 will be kept apart of the atmosphere by injecting it under surface.

CO_2 retention under the surface must be long enough (in order of centuries or one millennium) until the global atmospheric CO_2 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.** This can be realized in various depths from 600m down to 3000 m and more.

ENVIRONMENTAL BENEFITS OF 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 annual growth of 2% annually and reached amount of 24 Gigaton/year CO_2 in 2001 [one gigaton (1 Gt) = 10^9 (one billion) metric tons (Mt)]. This is adequate to 6.5 Gt/year in _carbon equivalent_.

More than half of this amount, 3.5 Gt/year, 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_2 flux caused that the CO_2 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 earth surface has increased by 0.8°C.

Before this change occurred the temperature and CO_2 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 up to 80% of all energy production for a long time.

TECHNOLOGICAL PROCESS OF CARBON CAPTURE

Many of commercial technologies for CO_2 capture have seen applications as components of industrial processes. CO_2 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_2 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 (diisopropanolamine)
>   - ✓ 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_2 capture in bulk quantities to date. The only reasons why they have not been used for CC&S purposes yet are the relatively high costs.

Results of research & development studies indicate that _chemical_ absorption more suitable for post-combustion de-carbonization while _physical_ absorption fits better to pre-combustion de-carbonization.

CHEMICAL SOLVENTS

Alkanolamines are considered as best candidates for the post-combustion de-carbonization of flue gases.

They have been proven well as de-carbonization 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.
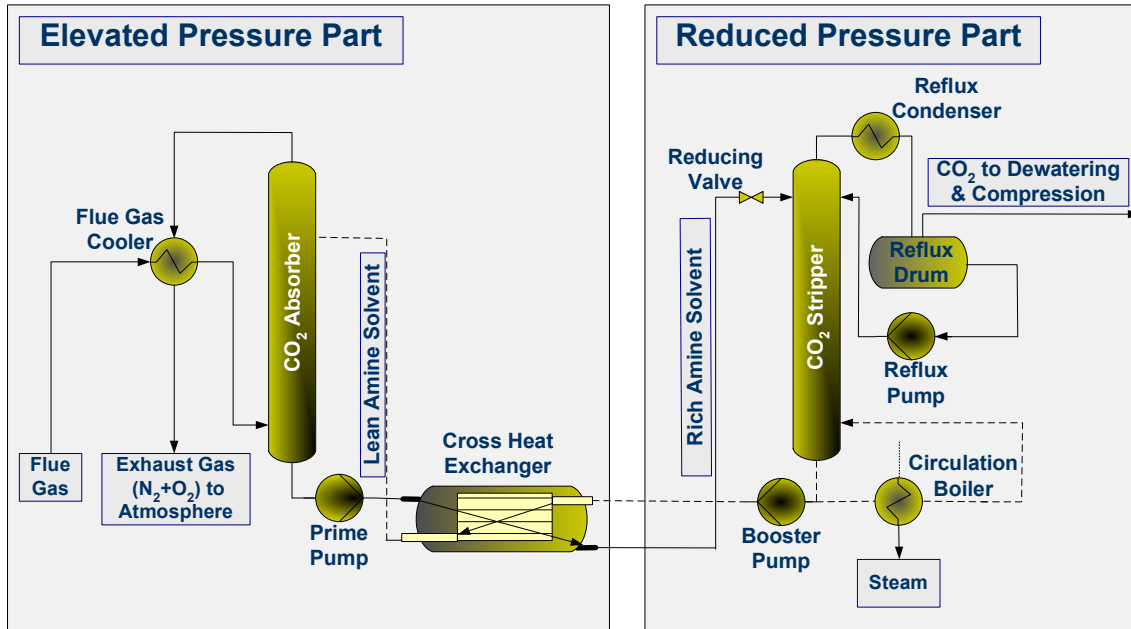
FIGURE 2
PROCESS FLOW DIAGRAM OF GENERAL FLUE GAS DECARBONIZATION SYSTEM

Upstream the absorption stage the CO_2 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_2 is chemically bound with the solvent by the exothermic reaction of CO_2 with the amine functionality of the solvent.

The liquid amine CO_2–rich solvent leaves the bottom of the absorber passes into the stripping tower via Cross Heat Exchanger. In the CO_2 Stripper, it is heated with steam to liberate the CO_2 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_2 from the liquid.

CO_2 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 has been practiced in large scale in the natural gas processing industry to remove hydrogen sulfide (H_2S) and CO_2 from natural gas. Their direct adoption to flue gas de-carbonization has two problems.

First, CO_2 occurs in the flue gas in bulk quantity, while in natural gas only as an impurity. Second, de-carbonization of natural gas must address the presence of H_2S while there is no H_2S in flue gases.

The greatest issue in post-combustion de-carbonization is the low pressure (atmospheric) of the flue gas. Only chemical solvents with high reaction energies like alkanoamines can economically scrub CO_2 under such low partial pressures.

Generally amine is a group of organic compounds, which can be considered as derived from ammonia (NH_3) by replacement of one or more H_2 molecules by organic radicals.

Amines are classified according to the number of hydrogen's of NH_3 that have been replaced by radicals as follows:

> ➢ **Primary Amine** (RNH_2)
> ➢ **Secondary Amine** (R_2NH)
> ➢ **Tertiary Amine** (R_3N)

Primary Amines (RNH_2) include monoethanol amine (MEA) and diglycolamine (DGA). There is considerable industrial experience with Primary Amines chemical absorption solvents, especially with MEA.

MEA, one of the most frequently used solvents for CO_2 capture, has been the traditional solvent of choice for CO_2 absorption and acid gas removal in general. It represents the cheapest technique but it's capture reaction heat of 1.9 MJ/kg is the highest.

It's 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 CO_2 removal from the gas stream and also in the regeneration step.

Another drawback is the high reactivity with COS and CS_2 resulting in solvent degradation. Also the CO_2 causes high corrosivity, because CO_2 itself is a strong corrosivity agent.

Techniques based on primary amines were commercially used for example by Fluor Daniel ECONAMINE FG process, with MEA concentration of around 30wt% to successfully remove 80% - 90% of the CO_2 from the flue or ABB LUMMUS process which uses MEA concentration of around 20wt%.

Secondary Amines (R_2NH) include diethanolamine (DEA), di-isopropylamine (DIPA). Secondary amines have lower capture reaction heat and possess some advantages over primary amines.

For example the reaction heat with CO_2 of DEA is only 1.5 MJ/kg comparing to 1.9 MJ/kg for primary amines. In other words, the secondary amines require less heat in the regeneration step than primary amines.

It is therefore more economical in the regeneration step than MEA. However, it has all the other problems of primary amines.

Tertiary amines (R_3N) amines which include triethanolamine (TEA) and methyl-diethanolamine (MDEA) are even less reactive, with lowest heat requirements for CO_2 liberation from the CO_2 containing solvent (MDEA – 1.3 MJ/kg).

Tertiary amines react more slowly with CO_2, resulting in necessity of higher circulation rate of solvent compared to primary and secondary amines.

Tertiary amines are less sensitive to degradation processes and have also lower corrosion rates than primary and secondary amines.

PRE-COMBUSTION CARBON CAPTURE

Pre-combustion capture is the transformation of the fuel into a mixture of CO and H_2 through gasification, shift reaction or partial oxidation.

Technology of pre-combustion capture of CO_2 via gasification already exists as a well established industrial process. It is known as a technological segment of H_2 production processes commonly used and proven in NH_3 production, oil refinery or methanol (C_3OH) synthesis.

The water gas shift stage is usually in the center of the process. Double benefit of production of valuable H_2 in parallel with CO_2 separation step means added commercial value.

Another advantage of H_2 co-production is the possibility of fuel cells integration for power generation purposes, but also for transportation (in the medium-term outlook, H_2 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 fuel feedstock is shown in Figure 3.

Formula of technological sequence:

SYNGAS GENERATION BLOCK ⇨ WATER GAS SHIFT REACTOR ⇨ CO_2 CAPTURE ⇨ CCGT CY

The CO and H_2 mixture can be used as fuel in a turbine cycle, giving rise to a high CO_2 concentration stream, so that simple separation techniques can be applied.
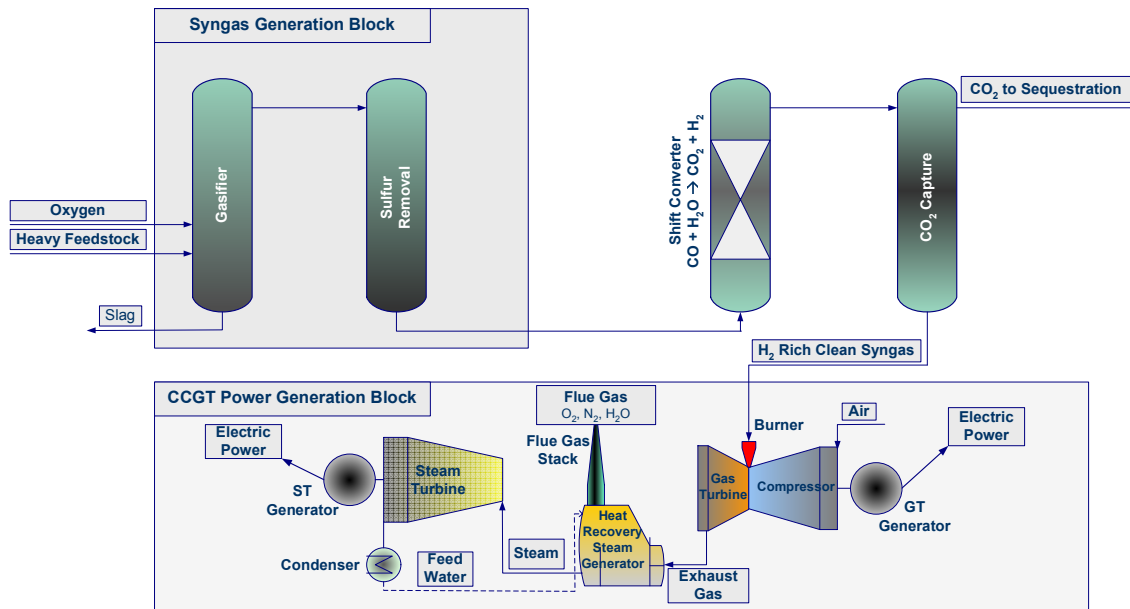
FIGURE 3

SIMPLIFIED FLOW DIAGRAM OF IGCC SYSTEM BASED ON HEAVY FUEL FEEDSTOCK

This configuration 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.
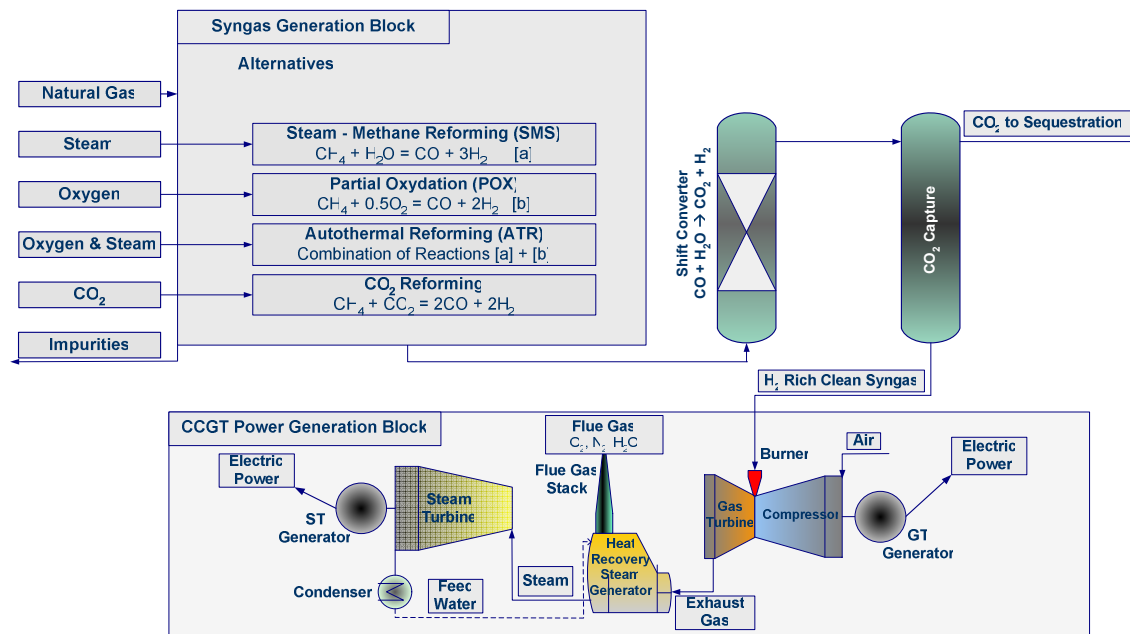
FIGURE 4

SIMPLIFIED FLOW DIAGRAM OF IGCC SYSTEM BASED ON NATURAL GAS WITH PRE-COMBUSTION CAPTURE OF CO$_2$

The difference between both schemes is in the utility sense of the IGCC concept itself. In the case of heavy fuel feedstock (coal, petcoke, petroleum residue, etc.) 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 CCGT (Combined Cycle Gas Turbine) would be preferable instead.

The fact that in both cases the gas turbine is fired with H_2 rich fuel deserves attention.

Commercial gas turbines are normally designed for natural gas or oil operation. Their compatibility to H_2 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_2 and highest possible amount of H_2. After the CO-conversion and removal of condensate, the gas mainly consists of H_2 with CO_2.

The CO_2 can then be separated by chemical or physical absorption for disposal or use. The H_2 can be used as a chemical feedstock, or as fuel in a CCGT plant or eventually a fuel cell.

Chemical or physical gas absorption equipped with a stripping regeneration stage, generally called as the **C**old **G**as **C**leanup – CGU has been used almost exclusively for the syngas de-sulfurization 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 de-carbonisation 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_2 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_2 in conventional combustion means that a large volume of gas has to be handled, resulting in large equipment sizes. Moreover, strong-afinity chemical solvents have to be used to capture such small concentrations of CO_2 in such a big volume.

Absorption of CO_2 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 strong chemical degradation sensitivity to SO2 an NO2 exists. In the presence of oxygen also their corrosion aggressiveness 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 Piemsa 2006 employ MDEA process. Reason for such massive deployment is that MDEA is highly effective with de-sulfurization of syngas.

Of course, this does not mean that the same competitiveness of MDEA will be reproduced in the future applications of the de-sulfurization ⇨ CO_2 capture ⇨ CO_2 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_2 concentration and pressure could be increased, the CO_2 capture equipment would be smaller and physical solvents could be used, with lower energy penalties for regeneration.

Exactly this is the case for CO_2 separation in pre-combustion capture processes applied to IGCC. Compare to combustion flue gases, in this case CO_2 concentration is 3 times higher while pressure upstream the gas turbine is typically 20 times higher.

Volume concentration of the CO_2 is therefore 60 times higher comparing to a typical coal flue gas. The advantage in this case is 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 pre-combustion CO_2 capture from IGCC plant based on heavy fuel gasification.

RECTISOL process with intermediate water-gas-shift offers multiple benefits, like:-

> ➢ de-sulfurization,
> ➢ additional H_2 generation via WGS,
> ➢ H_2 separation, and
> ➢ CO_2 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_2 separation.

The only exclusion is that no CO_2 capture has been realized in this case while the separated CO_2 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 de-sulfurization).

SELEXOL is another physical solvent competitive to RECTISOL. There are 55 SELEXOL operating units in syngas and natural gas service.

In relation to the de-sulfurization in IGCC, SELEXOL has fewer instances than RECTISOL.

On the other hand, as far as H_2 production or CO_2 capture is the priority, SELEXOL moderately outperforms RECTISOL.

List of references of this kind comprises several important refinery IGCC projects as indicated in Table 2.

| PLANT OWNER	COUNTRY	COD	FEEDSTOCK	GASIFICATION PROCESS	APPLICATION
SCE Cool Water	USA	1984	Bituminous Coal	Texaco	NH_3
Mitteldeutsche Erdöl Raffinerie	Germany	1985	Visbreaker Residue	Shell	C_3OH
Farmland Industries Inc.	USA	2000	Petroleum Coke	Texaco	NH_3
API Energia SPA.	Italy	2001	Visbreaker Residue	Texaco	IGCC
SARLUX srl	Italy	2001	Visbreaker Residue	Texaco	IGCC
Total Fina Elf/Texaco	France	2006	Refinery Residue	Texaco	H_2

TABLE 2
REVIEW OF SELEXOL APPLICATIONS IN GASIFICATION PROJECTS

Out of the six projects listed in Table 2 item entitled *Farmland Industries, Inc. Gasification – petroleum coke to* NH_3 is also one which meets criterion of a CO_2 *ready-to- sequestration* plant.

Farmland Industries have added petroleum coke gasification unit adjacent to its existing refinery in Coffeyville, KS. The new Gasification unit will produce a syngas for the production of NH_3.

Approximately 1,100 tons per day (TPD) of petroleum coke from the Coffeyville refinery is gasified to produce 1,100 TPD of NH_3. A portion of the NH_3 is subsequently upgraded to Urea-Ammonium Nitrate (UAN) solution.

Process flow diagram of its SELEXOL cleanup unit is shown in Figure 5.
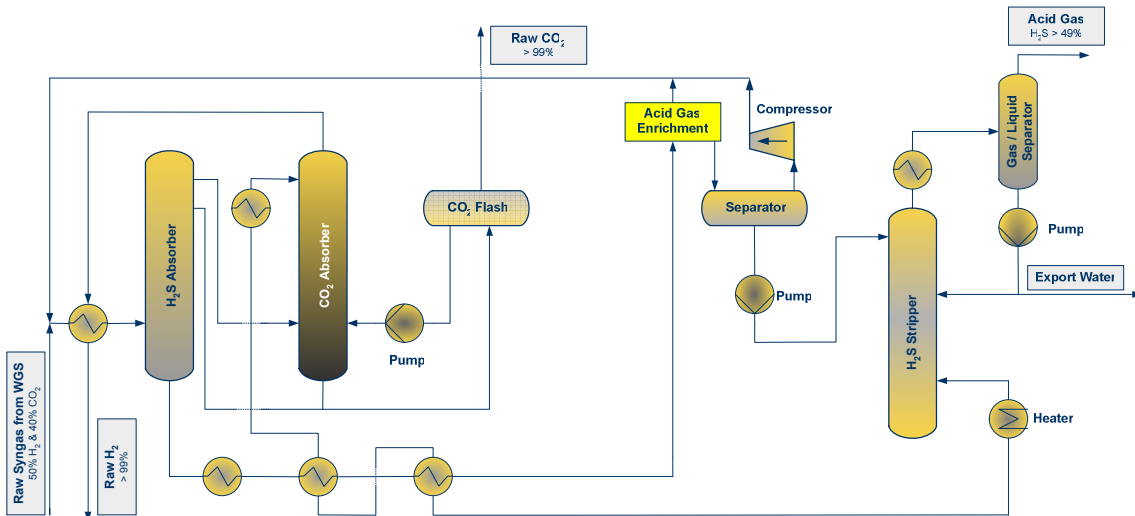
FIGURE 5
SIMPLIFIED FLOW DIAGRAM OF THE SELEXOL OF THE FARMLAND AMMONIA PLANT

The process is configured from two refining circuits. Triple effect of H_2 production, de-sulfurization and CO_2 separation respectively, can be won in this way. Acid gas leaves the H2S Stripper circuit with concentration $H_2S>45\%$, well enough to meet requirements of the downstream Claus process.

Raw CO_2 leaving the CO_2 flash tank is removed also in a state with *ready-to-sequestration* purity of 99%. The raw H_2 has purity 99.3%. Its final purification is performed in a downstream POLYBED Pressure Swing Adsorption (PSA) unit. (*POLYBED PSA units are used to separate impurities from natural gas at high recoveries and purities*).

It should be pointed out that the same as Farmland NH_3 plant any NH_3 technology can be formally construed as *carbon ready-to-sequestration* technology.

Such are for example all plants producing NH_3 or methanol reviewed in Table 1. Such are also any other plants producing CO_2 as intermediate product or byproduct in isolated form. The key product is H_2.

Wherever H_2 is generated via water-gas-shift reaction CO_2 is usually co-produced in considerable concentration. Unless it is used as further processing feedstock it offers potential to being sequestrated.
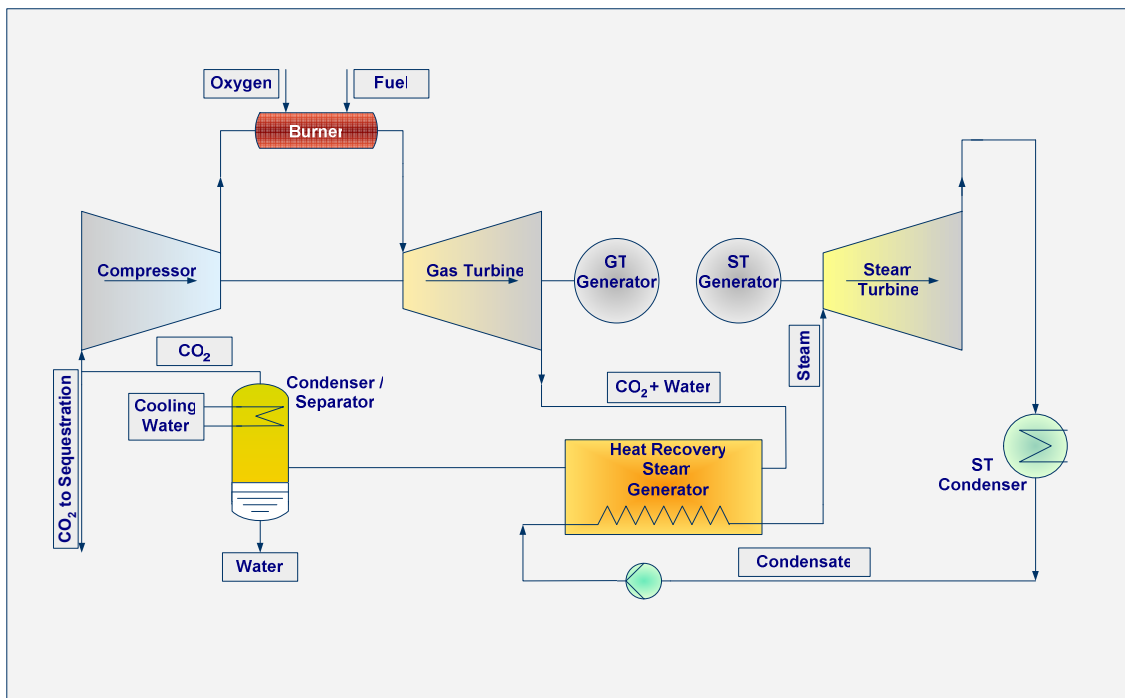
OXY-FUEL COMBUSTION

Oxidant is used in its concentrated form i.e. in the form of pure oxygen in oxy-fuel combustion.

Its advantage consists in the elimination of the CO_2 separation step. Instead, only water has to be removed from the flue gas by simple condensation.

The basic approach of oxy-fuel 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 oxy-fuel combustion incorporated in the combined cycle is shown in Figure 6.

FIGURE 6
OUTLINE OF OXY–FUEL COMBINED CYCLE SYSTEM WORKING IN SEMI-CLOSED CYCLE WITH CO₂ RECIRCULATION

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 CO_2 / H_2O working fluid.

➢ Control system precisely watching the stochiometric 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 CO_2 as the operating fluid impose bigger challenge than H_2-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 oxy-fuel principle is one in which water steam instead of CO_2 is used as the operating fluid. Such concept is shown in Figure 7.
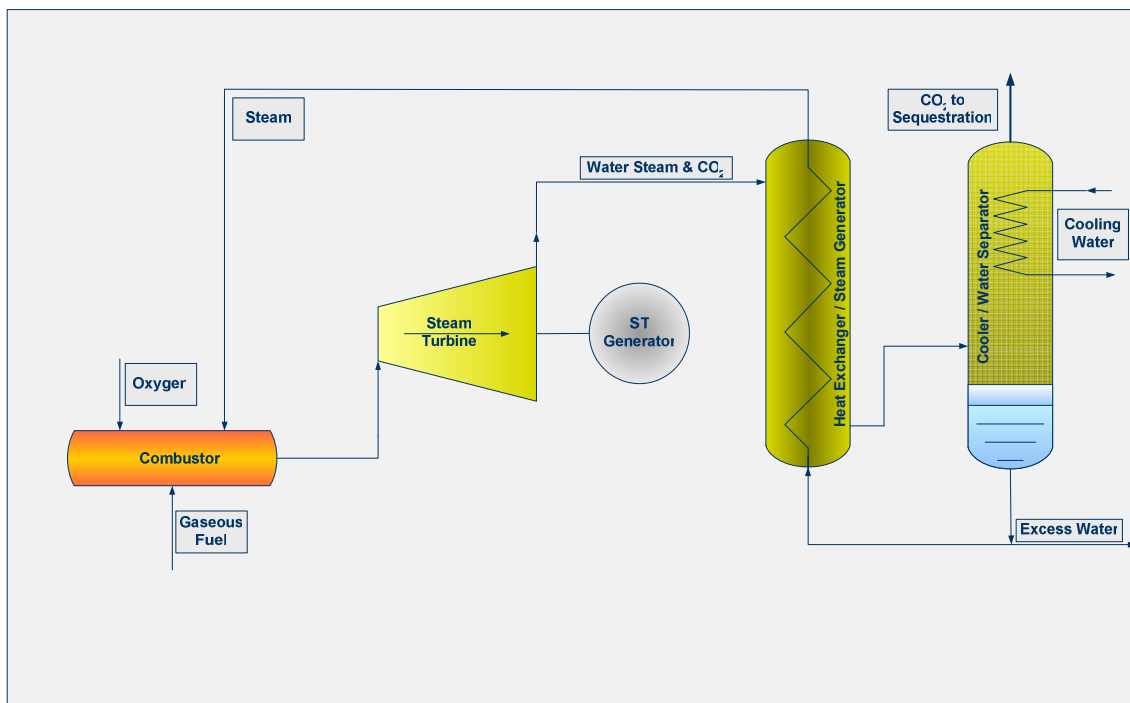
FIGURE 7
OUTLINE OF STEAM-WATER OXY–FUEL COMBUSTION SYSTEM

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_2 capture by means of the ion transport membranes;
- Chemical looping process;
- CO_2 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 800ºC to 900 ºC. 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_2 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_2 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 fueled 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_2 CAPTURE BY MEANS OF CHEMICAL LOOPING

Chemical Looping process makes possible to execute both fuel combustion and CO_2 separation in one gemini equipment. The process itself is a closed-circuit ion transfer, as shown in Figure 8.
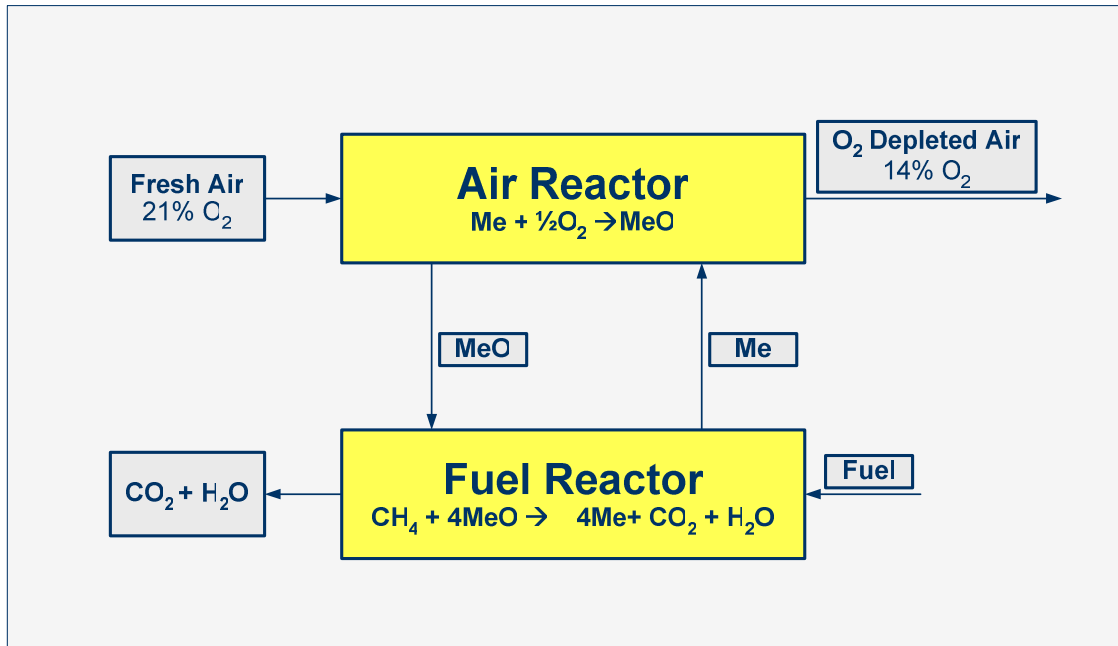
FIGURE 8
BASIC PRINCIPLE OF CHEMICAL LOOPING

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.
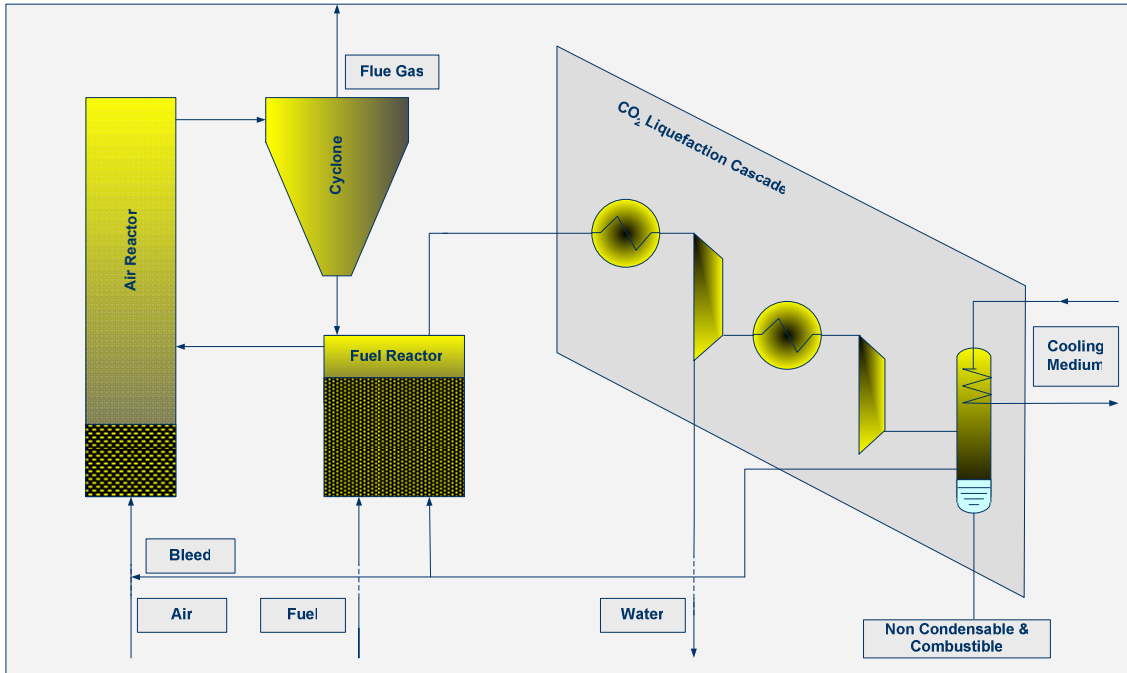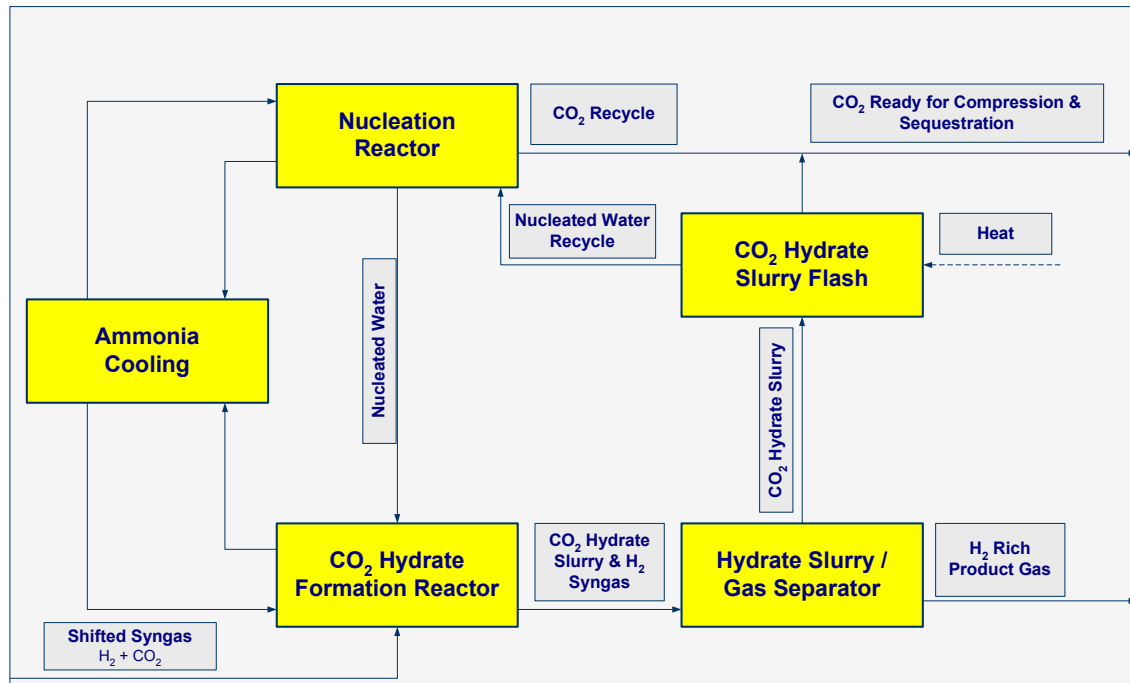

FIGURE 9
PROCESS FLOW DIAGRAM OF CHEMICAL LOOPING SYSTEM

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_2 + H_2O.

➢ 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 *pseudo-combustion* as well. Its advantage is that CO_2 is inherently separated off and no extra energy is to be expended for this purpose.

CO_2 HYDRATE PROCESS

CO_2 hydrate process is another example from the portfolio of CO_2 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 PROCESS FLOW DIAGRAM OF CO_2 HYDRATE PROCESS

The process is based on the absorption ability of water to create hydrates with CO_2 at high pressure and very low temperature. This requires NH_3 refrigeration. CO_2 is hydrated in the CO_2 Hydrate Formation Reactor with nucleated water coming from the Nucleation Reactor.

Nucleation process consist in creation of enough active centers called *nuclei* in a solvent, water in this case. In the further step the nuclei promote massive hydratation of CO_2 to give rise to hydrate slurry. In the next step CO_2 can be separated from its hydrate slurry on mild conditions.

The process promises good results in the economy of CO_2 capture with low penalty in the efficiency and low capital and operating costs.

CO_2 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

CO_2 storage in deep coal, gas and oil beds may be a promising pathway with agreeable kind of "geological sink" for storing CO_2 emissions in un-mineable coal, gas and oil beds.

At the same time the production of natural gas (CH_4) and oil from gassy coal and depleted gas and oil beds can be significantly increased. Outline of the arrangement and function of the CO_2 sequestration process in oil bed is given in Figure 11.
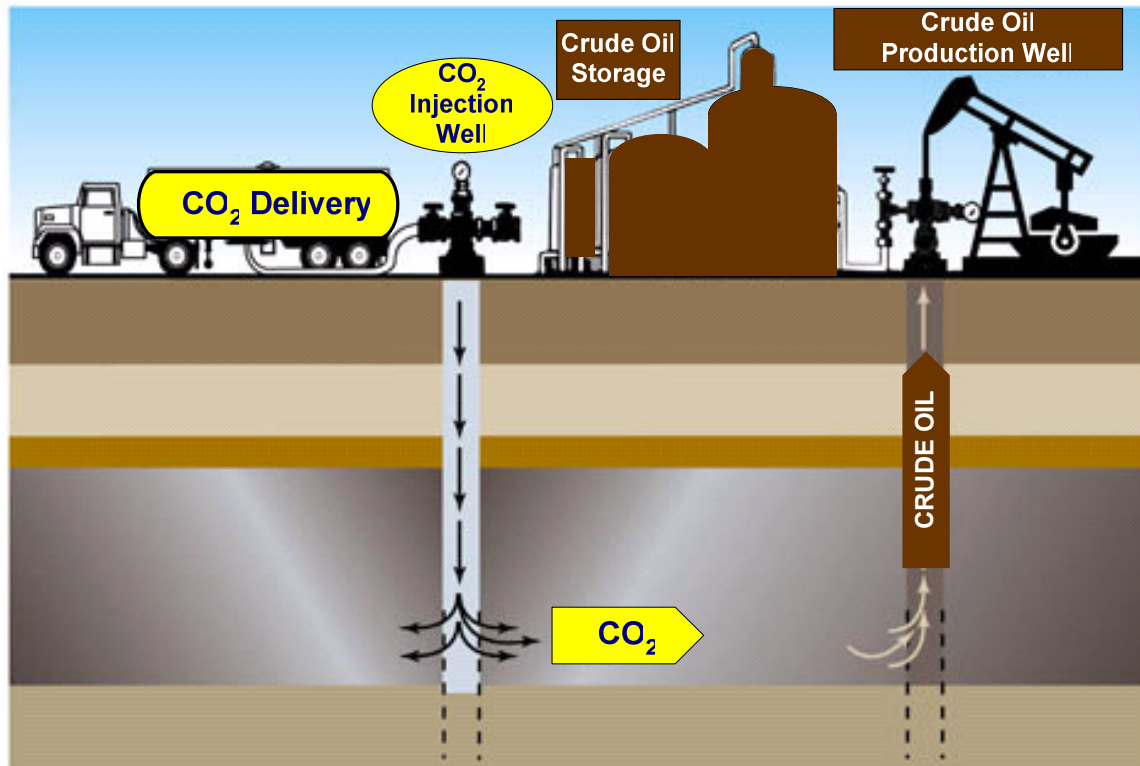
FIGURE 11
OUTLINE ARRANGEMENT OF THE CO2 STORAGE IN DEPLETED OIL FIELD

CO_2 storage in depleted oil and gas fields has an arrangement of CO_2 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_2 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 – 10,000Gt.

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, availability of natural renewable resources (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 targets in carbon emissions this appears impossible without massive implementation of the CC&S technologies in the future.