TNO Science and Industry

TNO-report

I&T-A R 2006/046

Denitrogenated combustion

Baseline processes and recent developments for power plants and industrial processes based on denitrogenated CO_2-capture

Report for CATO WP 2.3

Date	August 2006
Authors	N.A.M. ten Asbroek P.H.M. Feron
Order no.	004.35107/01.23
Keywords	Denitrogenated conversion Denitrogenated combustion Oxyfuel combustion Chemical-looping Combustion CO_2 capture
Intended for	CATO p/a UCE attn. E. Lysen Heidelberglaan 2 3584 CS Utrecht

Summary   Baseline processes and recent developments for power plants and industrial processes based on denitrogenated CO_2-capture (CATO)

The work described in this report is part of the activities in work package 2 of the CATO project.

This report presents the results of a study into the development status of denitrogenated combustion also called oxyfuel combustion for use in clean fossil energy production or also called Zero Emission Power Plants. The main objective of the study was to survey the known denitrogenated combustion processes and recent developments. The denitrogenated combustion concepts studied here are aimed at applications for the production of electric energy from fossil fuels without the emission of CO_2 and other greenhouse gases (clean fossil energy). A major benefit of denitrogenated combustion is that the combustion gas is composed of mainly CO_2 and water making the separation of pure CO_2 easy. In contrast to the separation of CO_2 from combustion gasses, the production of denitrogenated air (mainly oxygen) is not trivial. In fact in denitroginated combustion the separation problem for obtaining pure CO_2 has been shifted from post-combustion to the pre-combustion stage.

1: Post-combustion principle
2: Pre-combustion principle
3: Oxy-fuel principle = direct stoichiometric combustion with oxygen
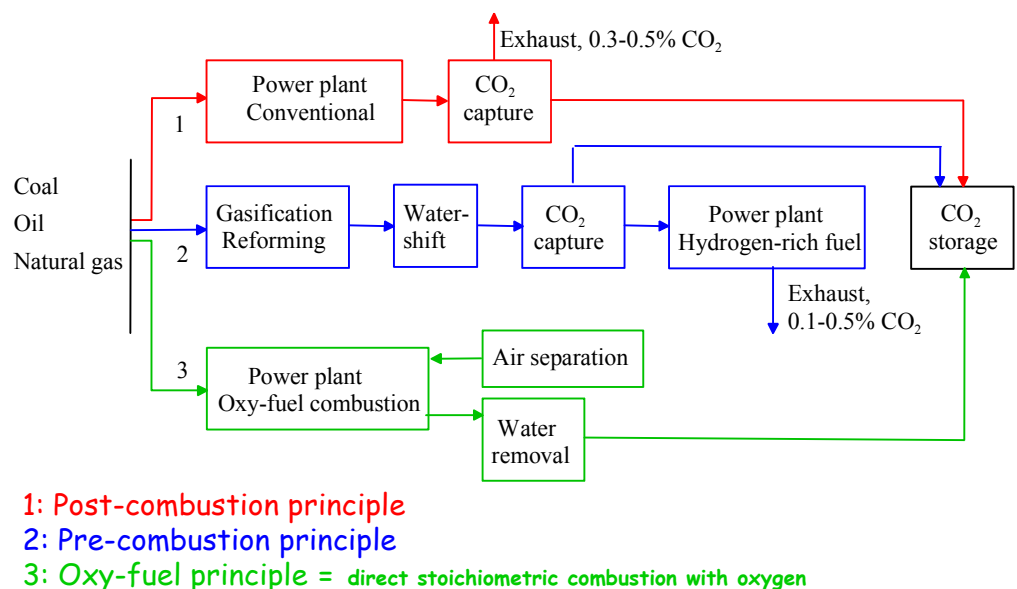
Figure 1.1   Different concepts of ZEPP's (Source SINTEF, NTNU, BP Oil, 2001).

Oxy-fuel technologies are a family of techniques involving some form of air-separation and the direct stoichiometric combustion of hydrocarbons with the separated oxygen. The baseline oxy-fuel combustion process consists of cryogenic air separation with hydrocarbon combustion in oxygen which is diluted with CO_2 to moderate the combustion temperature. This baseline oxy-fuel technology has

lower efficiency potential then post-combustion CO$_2$ capture with more complex processes and higher development risks. Some new novel oxy-fuel developments potentially are more efficient then post-combustion capture. But only under the conditions that significant improvements in these oxy-fuel technologies are made in order to reduce costs and technological developments in post-combustion capture stagnate. Large scale implementation of oxy-fuel in the near future is therefore doubtful. More stringed greenhouse gas abatement laws could however speed-up this implementation making the huge cost of replacing current power plant technology acceptable, as oxy-fuel technologies are very difficult retrofit able to current power plants.

For the some what longer timeframe Solid Oxide Fuel Cell (SOFC), Chemical Looping Combustion and Advanced zero emission power plant (AZEP) may become the preferred baseline technology for a Zero Emission Power Plant (ZEPP). These technologies promise attractive power plant efficiencies with CO$_2$ capture close or even better to near future state of the art power plants built according conventional design. There is however serious doubt if it will be economically or even possible to built a large power plant based on SOFC. Also the development of oxygen transfer membranes seems not as forthcoming as predicted. Stability and absolute flawless operation of the membranes during long operation is still not guaranteed. Furthermore AZEP and SOFC are relaying on gaseous fuels which are much more limited then solid fuels like coal. In order to operate these technologies with solid fuels, gasification of these solid fuels is required resulting in higher plant costs and a sharp reduction in plant efficiency. CLC has here a benefit, new developments aimed at direct integration of gasification in the fuel reactor of the CLC-CFB boiler. CLC-CFB technology is already very close to the well known CFB technology with potential for direct integration of solid-fuel gasification and further development to pressurised-CFB boiler technology. CLC-CFB is therefore the most promising oxy-fuel technology to be competing against post-combustion for application in a solid-fuel ZEPP in the near future. For gaseous fuelled power plants the new processes based on CLC look promising candidates.

List of abbreviations

CLC	-	Chemical-Looping Combustion
ZEPP	-	Zero Emission Power Plant
CAR	-	Ceramic Autothermal Recovery
AZEP	-	Advanced zero emission power plant
CES	-	Clean Energy Systems
CFB	-	Circulating Fluidized Beds
IGCC	-	Integrated Gasification Combined Cycle power plant
TIT	-	Turbine Inlet Temperature
OTM	-	Oxygen Transfer Membrane
CLC-CFB	-	Chemical-Looping Combustion Circulating Fluidized Beds
SOFC	-	Solid Oxide Fuel Cell

Table of contents

1.   Introduction in Denitrogenated Combustion

Denitrogenated combustion processes are processes where carbonaceous fuels are combusted in air with reduced nitrogen content (up to pure oxygen). Application of this technique in industry is in fact old and well known. It is commonly used in industrial processes where high temperatures are needed e.g. the melting of glass and iron. The highest temperature level of the combustion gases to be reached under stoichiometric combustion conditions is called the adiabatic flame temperature of stoichiometric combustion. Dilution by inert gases, e.g. nitrogen in case of stoichiometric combustion with air, reduces the adiabatic flame temperature compared to stoichiometric combustion with pure oxygen. For certain high temperature processes stoichiometric combustion with air results in an adiabatic flame temperature which is insufficient to perform the targeted industrial task. A common way to increase the required adiabatic flame temperature is by choosing a different fuel, an alternative or complementary way is to reduce the dilution effect of the nitrogen through combustion in oxygen enriched air.

In this report we limit ourselves to a class of denitrogenated combustion primarily aimed at electric energy production without emission of CO_2. This class of denitrogenated combustion is one of the routes which could lead to the goal of creating a Zero Emission Power Plant (ZEPP). An important denitrogenated combustion sub-class is combustion using pure oxygen as combustion agent. This denitrogenated combustion sub-class is most commonly called oxy-fuel combustion.

Oxy-fuel combustion has until recently not actual been considered for real application because of its much higher cost compared to conventional electric energy production. The renewed interested for oxy-fuel combustion lies in its inherent property to produce pure CO_2 from its combustion products using only a simple water condensation step. Pure CO_2 can be compressed and stored in underground pockets e.g. empty gas and oil fields. The ability to produce electric energy from fossil sources with storage of CO_2 is called "clean fossil energy production" and is now a hard sought quality because of CO_2 emission quota and reduction targets specified by the Kyoto treaty.

Oxy-fuel combustion however doesn't come cheap. The need for production of pure oxygen is in fact trading in the problem of separating CO_2 from flue or reformer gases for separating oxygen from air. Several technologies are available for the production of pure oxygen from air. However using current technologies, both the separating of oxygen or CO_2 are energy intensive and complex resulting in large electricity cost increase. In theory the power plant efficiency as a result of the separation of oxygen can be partly compensated for by higher power generating-efficiency because of higher working temperatures. However state of the art gas turbines and supercritical boilers are limited to working temperatures already now

attained with stoichiometric combustion of most fuels with air. The materials able to work at high temperatures are simply not available. Because of these material limitations, high adiabatic flame temperatures which occur during combustion with pure oxygen become an added problem in stead of a benefit. These flame temperatures may rise to 3500 °C when pure oxygen is used for combustion. The adiabatic flame temperature has to be limited in oxy-fuel power plants by diluting the combustion gases with an inert gas. Because pure CO_2 needs to be produced only dilution with CO_2 or steam are options. Thermodynamically cooling of combustion gases by water injection is less favourable then combustion in CO_2 diluted oxygen because of the phase change encountered by water when becoming steam. Furthermore, cooling by water injection results in changing of properties of the combustion gases. This means that the operating fluid is in-between steam and gas turbine conditions but at temperatures typical for a gas turbine. This is practically not feasible with current material technologies. Extensive water injection results in a fluid close to steam turbine conditions which can be operated with current technology but results in a lower efficiency. Therefore in oxy-fuel combustion dilution of the combustion gases is preferably performed by recycling a part of the produced CO_2 over the turbine or boiler system.

A second sub-class of denitrogenated combustion applicable as a ZEPP is Chemical Looping Combustion (CLC). Chemical looping combustion does not require a pure oxygen supply but uses intermediate particles which are oxidized in contact with air and reduced in contacted with the fuel. In most cases CLC particles are a combination of fine dispersed metal mixed with an inert carrier. Here the inert carrier has the function of providing a high metal surface area and strength to the particle a relative low cost. However also natural metal containing ores like Hematite or minerals like Calcium Sulphate are used [8, 23, 24]. In contrast to oxy-fuel combustion the separation of oxygen (oxidation of metal or mineral) produces heat, while the reduction of the particles with fuel is for most particulate material mildly endothermic. In the common form of CLC particles are transported between an oxidation and a fuel reactor using interconnected fluidized beds. The heat absorbed by the recycling spent/fresh particles helps to moderate the overall combustion temperature. The produced combustion gases contain mainly CO_2 and H_2O but also some minor other impurities originating from the fuel.

2.   Denitrogenated combustion as clean fossil technology

2.1   Oxy-fuel combustion and Chemical Looping as ZEPP

Oxy-fuel combustion and Chemical Looping are technology routes which could lead to the goal of creating a Zero Emission Power Plant (ZEPP). The combustion products of these processes consist mainly of carbon dioxide and water vapour, this translates to about 80% to 98% CO_2 after water separation. The actual attainable CO_2 purity depends strongly on the fuel used and the particular oxy-fuel combustion process.

Like most other ZEPP concepts the concentrated CO_2 stream produced by oxy-fuel combustion and CLC have to be upgraded before transport and disposal in e.g. aquifers or depleted oil & gas fields. This upgrade involves compressing the gas, drying and further purification before delivery into a pipeline. The main impurities present in the upgraded CO_2 are acid gas components such as SO_2, SO_3, NO, NO_2 and HCl derived from the fuel used and inert gas components, such as nitrogen, argon and oxygen, derived from the oxygen feed. Ideally the CO_2 is transported in a pipeline as a dense supercritical phase. In case where the transport pressure is near the critical pressure of CO_2 it is important to limit the concentration of inert gases in order to avoid increasing the critical pressure of CO_2 to be transported. In general a limit of 3 wt% inerts in CO_2 to be transported and stored is used. A high inert content has the danger of developing a two phase flow during transport resulting in high compression cost, the 3 wt% limit therefore represents a general accepted optimum between compression cost and additional costs for further up-grading of the produced CO_2. For many storage options acid gas components need to be removed to comply with legislation covering co-disposal of toxic or hazardous waste or to avoid environmental problems. Especially in the case when CO_2 is used for enhanced oil or gas recovery pollution of the hydrocarbon stock by these acidic components is undesirable. The carbon dioxide must also be dried to prevent water condensation and corrosion of conventional carbon-steel pipelines.

2.2   Thermodynamic cycles for Oxy-fuel power production

The Oxy-fuel and CLC combustion reactors are the core of the zero emission power plant concept based on these technologies. However to produce power these reactors will be part of a larger process scheme, incorporating a thermodynamic. Three different thermodynamic cycles are considered as basis for these process schemes [33].

Indirect Heating-Rankine Cycle
The oxy-fuel or CLC combustion reactor provides heat to a separate fluid by heat transfer using a heat exchanger according to a classical Rankine steam power

cycle. The Rankin steam power cycle is the most common form of this thermodynamic cycles using water heating to generate power (the Rankine cycle is already in widespread use today). This indirect thermodynamic cycle can be used with any hydrocarbon or carbon containing fuel.

Direct heating – Brayton Cycle

Oxy-fuel combustion takes place in a pressurised CO_2 rich recirculating stream in a modified gas turbine. The hot combustion gas is expanded in the turbine producing power. The sensible heat left in the combustion gases after expansion is transferred by a heat exchanger for use in a Rankine steam cycle. CO_2 and water vapour are subsequently separated by condensing the water vapour through further cooling. The CO_2 rich gas is compressed in the compressor section where a part of the CO_2 is recycled and the rest discarded.

CLC combustion takes place in a modified gas turbine were the combustion chamber is replaced by the oxidation reactor of the CLC system. Pressurised air is delivered to the oxidation reactor by the compressor where the oxygen reacts with the metal particles releasing heat. The hot air depleted in oxygen is expanded in the turbine producing power. The sensible heat left in the hot air after expansion is transferred by a heat exchanger for use in a Rankine steam cycle. Spent particle are subsequently transferred to the reduction reactor where gaseous fuel is used to reduce the particles. CO_2 and water vapour formed during reduction are subsequently separated by condensing the water vapour through further cooling. The resulting pressurised CO_2 rich gas is further compressed in the compressor section and discarded.

Only gaseous fuels like natural gas, light hydrocarbons and syngas ($CO+H_2$) can be used as fuel in the direct heating Brayton cycle.

Direct heating – Rankine Cycle

The fuel is combusted in a stream of pure oxygen, and the temperature is moderated by direct injection of water. The resulting steam plus CO_2 mixture (about 90% H_2O, 10% CO_2) is expanded in a turbine. In a condenser CO_2 and water vapour are subsequently separated. Gaseous fuels like natural gas, light hydrocarbons or syngas ($CO+ H_2$) can be used as fuel.

Currently the choice of thermodynamic cycle to be used depends largely on the fuel available. Direct heating Brayton cycles potentially render using oxy-fuel combustion and CLC the most efficient power generating processes. However because of the complexity and associated high cost of solid fuels gasification power production from solid fuels is most economical with an indirect heating Rankine cycle. However in the near future with improved lower cost reformer technology a direct heating Brayton cycle may become an alternative. The switch to using oxy-fuel combustion or CLC could then be a logical further evolution.

2.3   Oxy-fuel combustion technologies

The most attractive property of oxy-fuel combustion is the easy separation of CO_2 and other pollutants from the flue gases, facilitating efficient and clean disposal of these substances. However this requires the generation of pure oxygen, which is technologically complex and costly. Oxygen production through air-separation is mostly more economical then oxygen production by electrolysis. Current air separation methods for oxygen production considered in oxy-fuel combustion comprise cryogenic distillation, adsorption using multi-bed pressure swing units and membranes.
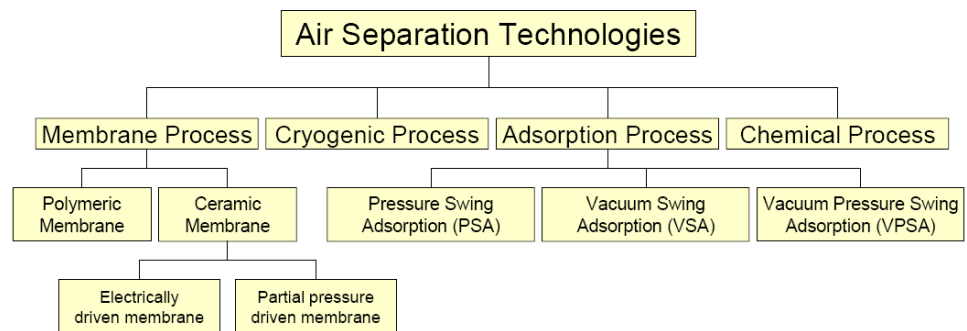
For oxy-fuel conversions requiring less than 200 metric t/day O_2, adsorption systems have proven to be the most economic. For all the larger applications, which include power station boilers, cryogenic air separation is currently the most economic solution [22]. Membrane processes have the potential to become the preferred future technology for oxygen production, however membranes are currently not enough developed to challenge the established technologies.

The potential benefits of oxy-fuel combustion for use in a ZEPP but also the drawbacks sparked considerable research into this subject. Several processes are now under research aimed at improving oxygen production or solving the problem of material limitations in power generation. These efforts result in a diverse pallet of process schemes all part of the oxy-fuel family but with unique aspects. In general oxy-fuel technologies can be divided into two main branches; the first are technologies based on cryogenic (low temperature) oxygen production, the second cover technologies based on high temperature oxygen generation. The low temperature technologies are more mature and on component bases already commercial proven, the high temperature oxygen generation can however be better integrated with a power cycle leading to more efficient power production. In this paragraph the members of the oxy-fuel family will be discussed.

2.3.1 Oxy-fuel based on cryogenic air-distillation

Oxygen production using cryogenic air-distillation combined with power production through combustion of fuel in a mixture made of oxygen and recycled CO_2 can be regarded as the baseline of oxy-fuel combustion.

Cryogenic air-distillation (Figure 2.1) is a technique already used for many years for the production of industrial gases like oxygen, nitrogen or helium from air. It involves compressing (up to 6 bar), drying and cooling down air to cryogenic temperatures (− 185 °C) followed by separation in several fraction based on boiling point in a distillation column.
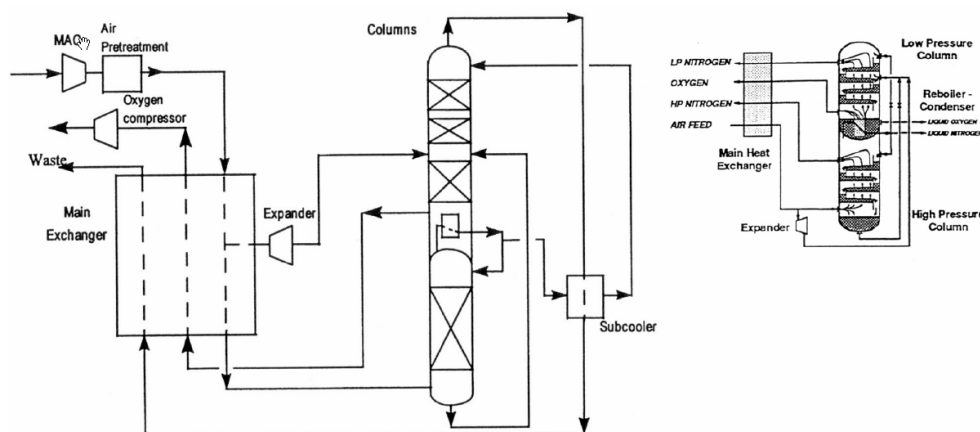

Figure 2.1   General process scheme of a cryogenic air separation plant.

Cryogenic air-distillation is a mature and proven technology producing high purity oxygen (up to 99.99%). Industrial sites exist with cumulative oxygen production of 30000 t/d based on cryogenic oxygen production. The largest single train cryogenic oxygen production plant in the world is operated at a capacity of 4000 t/d. Existing technologies would allow capacity up to 5000 t/d, while design studies for 7000 t/d single train unit have been performed.

Cryogenic oxygen production requires a substantial amount of power to produce pure oxygen resulting in direct reduction of the power available for delivery to the power distribution net. In addition to the reduced revenues in power delivery, substantial costs are made in the cryogenic distillation equipment needed to produce pure oxygen. Cryogenic distillation equipment is rather specialised and complex equipment resulting in significant investment, maintenance and operating costs. Because of the specialised knowledge needed to design, operate and maintain cryogenic industrial gases producing facilities even big industrial sites like chemical plants, refineries or big factories outsource mostly this work to special industrial gas supplier firms. Industrial gas producing facilities are found at nearly all big industrial sites requiring substantial amounts of pure gases. These facilities are almost exclusively based on cryogenic air-distillation technology.

2.3.1.1 Conventional power plant with combustion in recycled CO₂

The basic and most simple oxy-fuel combustion cycles involves the adaptation of conventional boilers or combined cycles using a CO_2 recycle to moderate the combustion temperature. Compared to the conventional power generating cycles without CO_2 capture a significant reduction in efficiency is measured caused by the power requirements for oxygen production and CO_2 recycling.
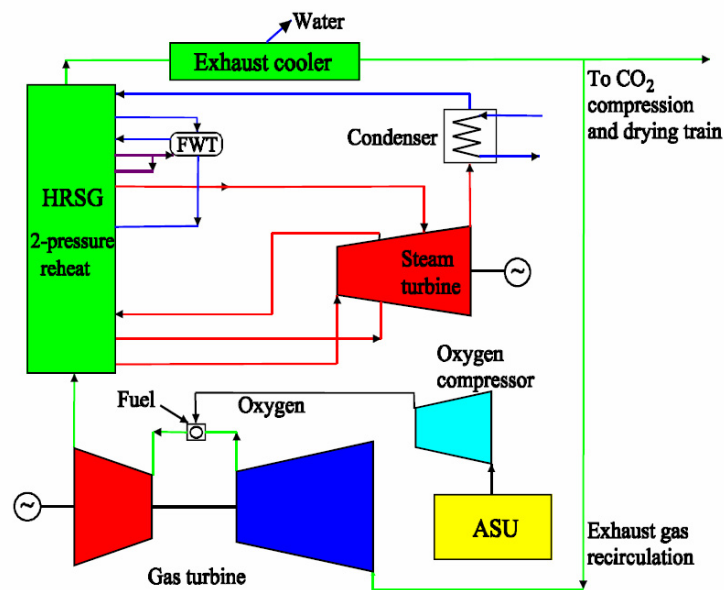

*Figure 2.2   Process scheme for an oxy-fuel combined-cycle power plant
(Source Bolland, Internet).*

Components for an oxy-fuel power plant based on cryogenic air-separation, a conventional power cycle and combustion temperature moderation through CO_2 recycle are all available.
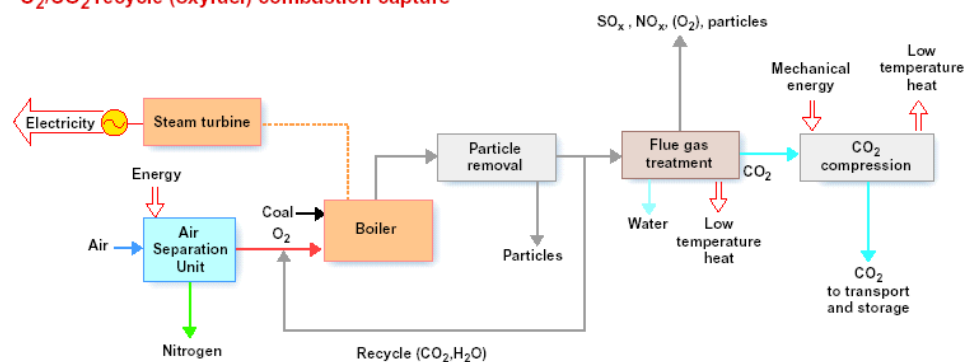
*Figure 2.3   Process scheme of Oxy-fuel combustion with CO_2 recycle for coal
(Source Vattenfall).*

Combining all components into a working industrial scale power plant has still to be proven. Concluding can be said that this option is the most mature and less risk oxy-fuel option, which should be considered as the base case in oxy-fuel combustion.

2.3.1.2   The Clean Energy Systems (CES) Oxy-fuel combustion concept

A novel oxy-fuel scheme using cryogenic produced oxygen, is a process by CES [14], employing a direct heating Rankine thermodynamic cycle. The CES technology targets the problem of excessive temperatures during combustion by reducing flue gas temperature through injection of water. The scheme proposed by CES uses an adapted rocket engine which combusts a liquid or gaseous hydrocarbon (mostly natural gas) with pure oxygen under almost stoicheometric conditions. A rocket engine is a relative simple device which because it doesn't rotate can be optimised for accepting very high temperatures. The produced high temperature (up to 4000 °C) combustion gases are cooled by injecting water in the combusting nozzle, before they reach the turbine, resulting in a mixture of 90 vol.% superheated steam and 10 vol.% CO_2 with a temperature of approximately 650 – 1600 °C and a pressure up to 500 Bar. CES claims that after expansion and condensing out the water, CO_2 with approximately 2% oxygen and some minor pollution remains, requiring no CO_2 upgrade facilities.

The concept being developed by CES consists of three units, shown in Figure 2.4:
−   Air separation
−   Fuel preparation
−   Power generation

Figure 2.4   The CES Oxy-fuel combustion concept (Source CES [26]).

Plants operating on the CES principle require gaseous or liquid fuel free from solids or corrosion inducing components. Possible fuels are methane, natural gas, alcohol, hydrogen, gasified coal or biomass. The steam plus CO_2 generator is very compact but requires very precise control systems as start-up and increase to full flow in a preheated plant can take place in less than 2 seconds.

Studies performed by CES on the technology claim (theoretical) efficiencies as high as 55% with CO_2 capture depending on the process conditions used. However the properties of the working fluid produced by the gas generator differ significantly from normal flue gases. In the ideal case this saturated steam and CO_2 mixture should be expanded at the high inlet-temperatures up to 1300 °C of a gas turbine. There is however no gas turbine available which can handle this mixture at maximum operating temperatures and pressure. In practice the only turbine available for this working fluid mixture will be a steam turbine, working at lower temperatures (565 °C inlet temperature) and at reduced efficiency. In the CES concept no recycle of diluting gas is needed to lower the turbine gas inlet temperature which is beneficial regarding efficiency, however the lower efficiency of a steam cycle reduces this benefit significantly. At the current state of technological development the CES concept is not more efficient then oxy-fuel system using cryogenically produced oxygen and a CO_2 recycle.

The success of the CES concept depends on the development of a turbine capable of operating at high steam, high pressure and high temperature. However CES is not in the position to develop this new turbine and no turbine manufacturer seems willing or capable to develop this essential piece of equipment.

CES proved the gas generator concept in 2000 by running a 110 kW pilot at the University of California Davis. A 20 MW thermal gas generator was successfully operated with over hundred starts and durations of up to three minutes in early 2003. Current development focuses on a small scale (up to 5 MW electrical) ZEPP based on a conventional indirect heating steam cycle. This project is executed with the participation of the California Energy Commission, NETL, Mirant and Air Liquide and started delivery of power to the grid in March 2005.

An evaluation of the CES process reveals that for the technology to become a reality much more technology development and demonstration is needed on this proposed power cycle. However if a suitable turbine is developed then the CES technology has potential for low capital cost and good efficiency.

2.3.2 Oxy-fuel based on high temperature oxygen generation

Bottleneck in oxy-fuel combustion using cryogenic air-distillation is the huge power requirement through compressing and cooling associated with the oxygen production comprising 0.25-0.30 kWh/kg O_2. The consequent of this power consumption is a sharp reduction in power plant efficiency, compared to a conventional state of the art power plant without CO_2 capture, equivalent to a drop in efficiency from 60 to 45%. Oxy-fuel combustion using cryogenic air-separation is a technology nearing maturity, but it is only marginally more efficient then the more developed pre-combustion capture and less efficient then the mature post-combustion CO_2 capture technology.

For a ZEPP based on oxy-fuel to become a reality in the near future, it is evident that a more cost effective way of oxygen production has to be developed. Important development in this field are based on the properties of certain ceramic materials to transport oxygen ions through a dense ceramic membrane made from perovskites or similar materials and release very pure oxygen at high temperatures ranging from 600 °C to 1000 °C. These dense ceramic membranes are commonly known as Ion Transport Membranes (ITM) or some times Oxygen Transport Membranes (OTM).

Composition of these perovskites differs by application but there based on mixed metal oxides that have a crystal lattice structure [21]. The selectivity of these materials for oxygen is infinite, at least in theory. In practice this might be compromised by membrane imperfections (pinholes) and membrane module imperfections (leaks through potting material). The oxygen permeability is primarily controlled by the oxygen ion vacancies in the metal oxide lattice. A difference in oxygen activity across the ITM will cause oxygen molecules to ionise on the ceramic surface and pass into the crystal structure while simultaneously on the permeate side of the membrane, the oxygen ions give up their electrons and

leave the ceramic in the region of lower activity. An electron conduction path is provided through the metal ions in the lattice.

The most common ceramic membrane separation of oxygen from air at high temperatures is based on the driving force of divergence in partial pressure ratios and uses a perovskites material with mixed ion and electron conductivity, as illustrated in Figure 2.5.
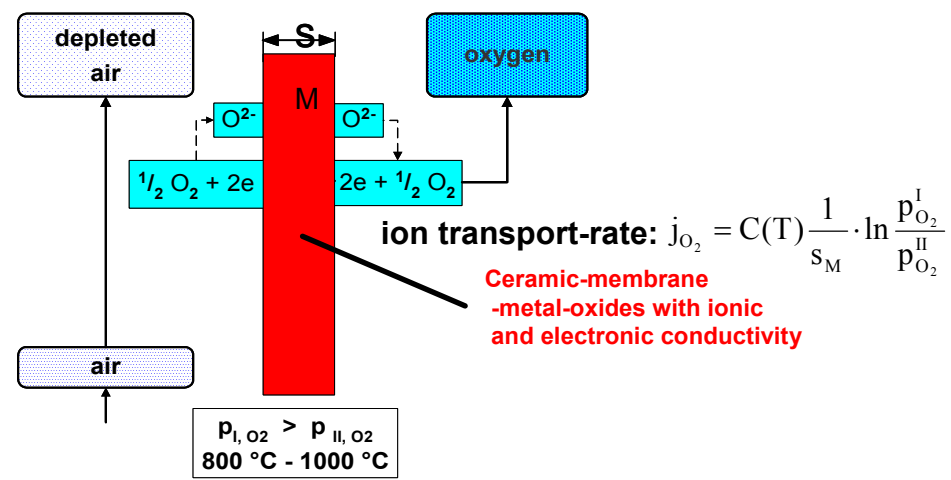

ion transport-rate: $j_{O_2} = C(T) \dfrac{1}{s_M} \cdot \ln \dfrac{p_{O_2}^I}{p_{O_2}^{II}}$

Ceramic-membrane -metal-oxides with ionic and electronic conductivity

$p_{I, O2} > p_{II, O2}$
800 °C - 1000 °C

Figure 2.5   O₂-production by a pressure-driven ceramic membrane (Source SINTEF).

The further development of oxy-fuel combustion concepts using ITM rely heavily on the development of selective membranes and leak-free membrane modules for high temperatures. ITM membranes are dense and a common drawback is the low membrane permeability.

In addition to the pure pressure swing driven processes also combined pressure and temperature or electric swing processes are employed. A combination of pressure and temperature swing is employed by the CAR process, which involves the alternated loading and unloading of a bed of perovskites particles with oxygen. Pressure swing processes involve oxygen transfer over a dense ceramic membrane integrated in a boiler or into a gas turbine (AZEP). Electric swing is employed to separate oxygen from air using a dense perovskites membrane integrated into a fuel cell, this process is called Solid Oxide Fuel Cell (SOFC).

2.3.2.1   CAR (Ceramic Autothermal Recovery)

The CAR concept is an alternative to ceramic membrane technology and utilises the oxygen storage properties on perovskite type materials at high temperature rather than oxygen transport properties. CAR is a development of BOC and is their contribution to the EU-project ENCAP where CAR is evaluated against other high

temperature oxygen production technologies using perovskites type of materials. The process involves two step; step 1 is the storage of oxygen in perovskites particles at high temperature, step two involves the release of oxygen from the perovskites particles at elevated temperature under sweep gas conditions. The process consists of cyclic operation of two beds containing the perovskite material in spherical pellets or in cylindrical extruded form. One bed is fed with a high temperature air stream and the oxygen is stored and retained in the material while in the other bed the oxygen is released by reduction of partial pressure, as illustrated in Figure 2.6. Release of oxygen is accomplished by sweeping the loaded bed with re-circulated combustion gases. Alternated operating of the two beds results in a sweep gas mixture enriched with oxygen.

Figure 2.6   O$_2$-poduction by CAR process (Source BOC).

Main driving force for the process is pressure swing through dilution with a sweep gas, however some temperature swing may also be involved by employing different temperatures for loading and unloading of the beds.

The process exhibit properties of a hybrid between Chemical Looping Combustion and Temperature Swing Adsorption (TSA) and is quit similar to the fixed bed approach being researched by TNO based on chemical looping technology (discussed in section 2.4 of this report). This becomes even more evident as the latest developments seem to indicate that BOC is also considering direct combustion in the oxygen releasing bed of gaseous fossil fuels. The CAR process and the fixed bed chemical looping technology exhibit similar technical problems to be solved. As in chemical looping the binding of oxygen in CAR is very selective and therefore the separation efficiency of oxygen en nitrogen is very high. Both technologies use high temperature oxygen generation which in potential could be integrated very efficiently into a power plant, resulting in a potentially more efficient power generating plant compared to oxy-fuel based on cryogenic air-separation. However this technology needs much more development before it is mature and industrial ready. Possible problems involve the control of hot gas streams between different reactor beds and thermal stress induced on the equipment by constant changing temperatures.

2.3.2.2 AZEP (advanced zero emission power plant)

A very attractive option for an ITM is the possibility for close integration with power generating processes, reforming them into a ZEPP. AZEP is such a decarbonisation processes based on denitrogenation employing reactor-integrated oxygen transfer. The process is under developments by Alstom/Norsk Hydro and has been supported by a 3-year EU funded project which started January 2002. AZEP employs ITM's to contact air directly with a gaseous fuel, as shown in Figure 2.7, with a Combined Cycle power plant.
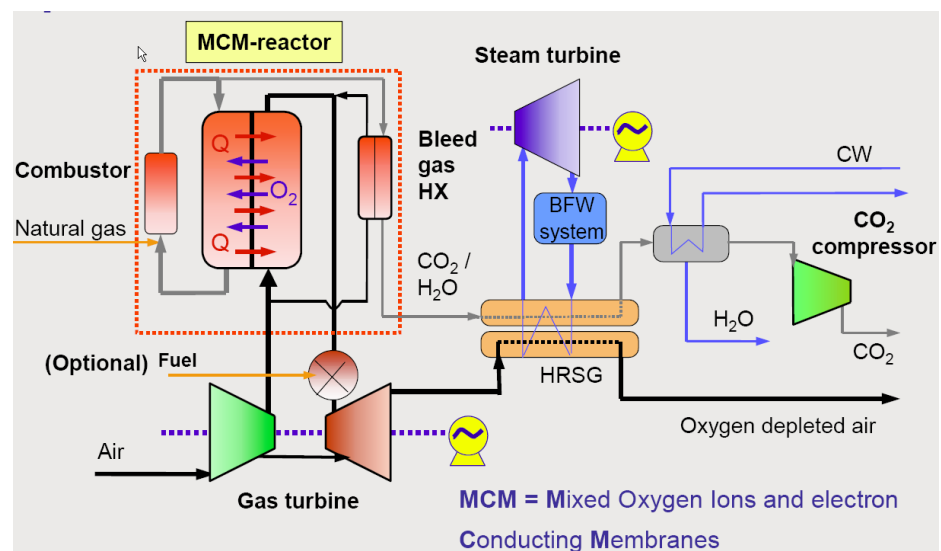

Figure 2.7   The AZEP oxy-fuel combustion concept (source Norsk Hydro).

In AZEP air is compressed and then fed to the hot up to 1200 °C ITM. Differences in oxygen partial pressure drive the transfer of oxygen through the membrane where the released oxygen is swapped away by the hot combustion gases coming from the combustor. The oxygen containing combustion gases are then enriched with natural gas and burned in the combustor. The major part of the reaction products (CO_2, H_2O) are re-circulated over the ITM as sweep gas while a smaller part is removed from the system for storage of CO_2. The heated air coming out of the ITM module, which is depleted in oxygen, is then expanded in a turbine and heat recovery steam generator, producing power. Optional the air leaving the ITM could be further heated by afterburning using the residual oxygen in the air and producing a gas stream better matching the optimal working temperatures of state of the art gas turbines (TIT > 1400 °C). The penalty when employing afterburning is lowering the CO_2-capture ratio of the AZEP plant to approximately 85%, however with an improved plant efficiency which according to studies [28] could be only 2-3%-point lower then a state of the art reference plant without CO_2-capture.

2.3.2.3 High temperature Solid Oxide Fuel Cell (SOFC)

Solid Oxide Fuel Cells are electrochemical devices operating a high temperature (1000 °C) that directly convert chemical energy, from a reaction between a fuel and an oxidant, into electrical energy. A SOFC can employ different fuels, such as hydrogen, ethanol, methanol, or gaseous fossil fuels like natural gas or gasified liquid or solid hydrocarbons. The SOFC consists of an electrolyte phase in intimate contact with an anode made of perovskites (negative electrode) and a porous cathode mostly based on nickel or nickel/ceramic composite materials (positive electrode), as shown in Figure 2.8.
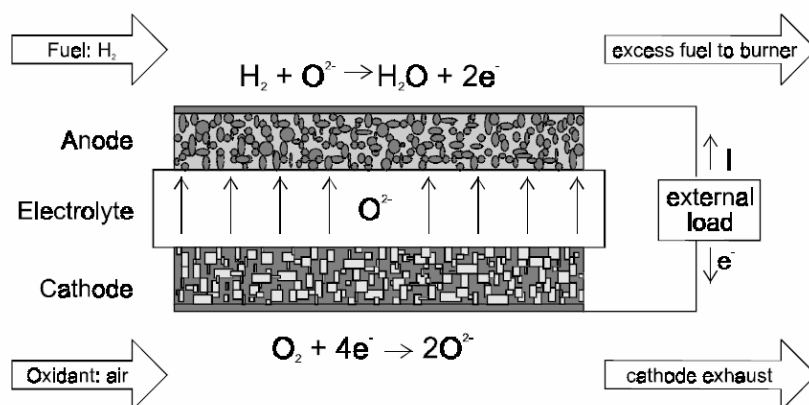

Figure 2.8   The working principle of a SOFC (source Thesis B. de Boer [25]).

The fuel and oxidant gases flow along the surface of the anode and cathode, respectively, and react electrochemically in the three-phase-boundary region established at the gas / electrolyte / electrode interface.

SOFC employs perovskite materials as cathode for ionising oxygen en serving as an electron guiding path. The electrolyte serves the purpose of guiding the oxygen ions from the cathode to the anode while at the same time repelling the transfer of electrons. At the anode a reaction occurs between the fuel and the oxygen-ion which results in the formation of water en the release of electrons. The anode is porous to facilitate the transport of fuel to the three-phase-boundary region where the reaction occurs and the removal from the reaction region of formed water. The anode material is often nickel or nickel/ceramic composite but also noble metals and cobalt could be used. Nickel is however mostly preferred on grounds of its good stability under high temperature reducing conditions, catalytic function in enhancing the anode reaction and cost. Electrons released during the oxidation of the fuel are guided trough an external pathway connected to a load and picked-up at the Cathode side where new ionisation of oxygen can take place. The high operating temperature of a SOFC is needed to obtain sufficient oxygen iodization and transport in the ceramic materials used as electrolyte and Cathode, furthermore the high temperature benefit the catalytic reactions taking place at the Anode.

Further development of the oxygen transfer membranes (OTM) and membrane materials is part of the EU-project ENCAP where the OTM technology is evaluated against other high temperature oxygen producing processes like CAR and other ion transport membrane based processes. Although SOFC is not strictly part of ENCAP the development of the OTM materials en membranes will benefit the development of SOFC.

SOFC are already very efficient power generating devises at small scale. However to generate large amounts of power in combination with CO_2 capture SOFC is best combined into a hybrid thermodynamic scheme (Figure 2.9). This hybrid scheme is formed by SOFC in combination with a gas turbine. The process looks like AZAP in that the SOFC works like the combustion chamber of the gas turbine however without a steam cycle. The SOFC + GT hybrid cycle produces directly power like a fuel cell in combination with the generation of power by a gas turbine. Very high thermodynamic efficiencies of 66 % [28] with CO_2 capture are expected, which is even better then an advanced combined cycle without capture of CO_2.
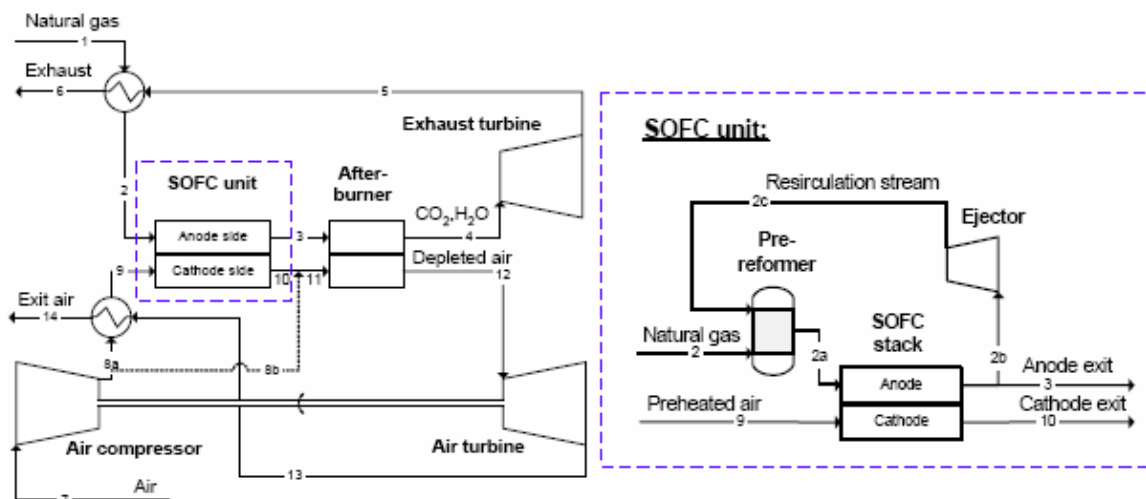

Figure 2.9   SOFC and gas turbine hybrid cycle [29].

The hybrid SOFC + GT has high potential to become an important technology for the construction of a ZEPP. Siemens has demonstrated at the University of California USA on a scale of 220 KW the hybrid SOFC + GT scheme (Figure 2.10).

*Figure 2.10   SOFC and gas turbine hybrid demonstrator
220 KW at the University of California
[Source Siemens internet [31].*

SOFC are however complex and costly devices where membrane stability is still a problematic issue. Furthermore for complete fuel conversion, which is required for CO_2 capture and high efficiency, some form of afterburner is needed to completely oxidize the remaining fuel. This afterburner itself can be an SOFC however requiring a large area of SOFC to completely oxidize the fuel [29].

SOFC currently is employed in natural gas fuelled power cycles. However in combination with gasification potentially coal or biomass could also be used in a SOFC + GT cycle. Although here the efficiency is expected to drop significantly because of the required oxygen production for gasification of these fuels and required clean-up of the syn-gas, however compared to current IGCC the efficiency is expected to be very good.

2.3.3   Other oxygen production technology

In addition to the already described oxygen production processes also adsorption and polymeric membrane oxygen production technology have been considered for oxy-fuel combustion. However the characteristics and performance adsorption processes or polymeric membranes make it difficult to efficiently integrate these processes with large scale oxygen consuming oxy-fuel power plants. Because of this these oxygen producing techniques are not much researched for application in oxy-fuel combustion.

Oxygen production based on adsorption processes like Pressure Swing Adsorption (PSA) or Vacuum Swing Adsorption (VSA) is a well established technique. PSA processes work on the principle of adsorption of gasses to a selective medium and can be categorized as equilibrium-based or diffusion-rate based.

Table 2.1   Relative strength of Adsorption of Typical Impurities [27].

Non-Adsorbed	Light	Intermediate	Heavy
H_2	O_2	CO	C_3H_6
He	N_2	CH_4	C_4H_{10}
	Ar	C_2H_6	C_5+
		CO_2	H_2S
		C_3H_8	NH_3
		C_2H_4	BTX
			H_2O

The most common form is equilibrium-based separation depends on the ability of the absorbent to absorb a greater amount of high absorption-affinity species then low absorption-affinity species at equilibrium. Diffusion-rate based processes separate components based on difference in diffusion-rate.

Adsorption processes use simpler equipment and is more energy efficient then cryogenic oxygen production. However adsorption processes produces less pure oxygen 90-96% because of the inability of the adsorbent to remove Argon from the oxygen product, which results in more inert gases in the produced CO_2 stream. In order to meet the generally used 3 wt% limit of impurities an oxy-fuel power plant using oxygen adsorption would therefore need an additional CO_2 upgrade technology to make the CO_2 suitable for transport and storage, which results in additional costs and energy consumption.

Adsorption processes are less flexible in scale-up compared to cryogenic air-distillation e.g. to production 95-96% pure oxygen instead of 90% one has to employ multiple beds of adsorbent resulting in significantly more bulky and costly equipment, while in case of cryogenic distillation only additional separation trays are needed. Furthermore when scaling-up adsorption processes to the scale needed for power plants application, one sees that the economics of scale in case of adsorption processes are less favourable compared to cryogenic air-distillation. This is caused by the fact that the cost of adsorption processes are for a large part covert by the adsorbents which are linear depended on the size of the plant, resulting in a high CAPEX for big adsorption plants compared to cryogenic air-distillation which becomes relatively more compact at higher throughput.
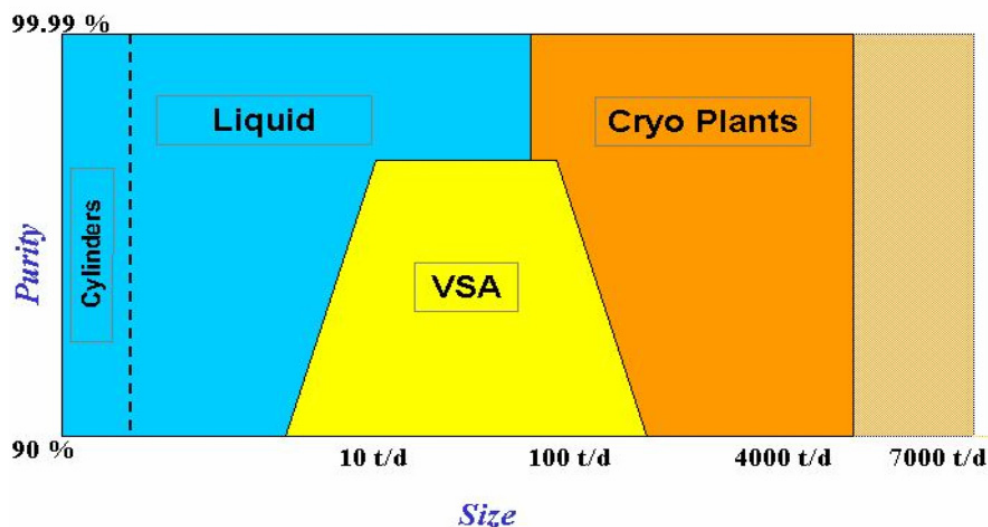
Figure 2.11   Oxygen production technology selection as a function of quantity.

It is shown that for oxy-fuel power plants requiring less than 200 t/day O_2, adsorption system will be economic. For all the larger applications, which include power station boilers, cryogenic air separation is the more economic solution [22]. As a consequence, cryogenic distillation is currently the only proved option for oxy-fuel combustion power plant at an industrial scale.

Polymeric membranes are a possible option for oxygen production but are not attracting much attention for application in oxy-fuel combustion. Commercially available polymeric membranes are, however, severely limited in selectivity and flux. This is shown in Figure 2.12.
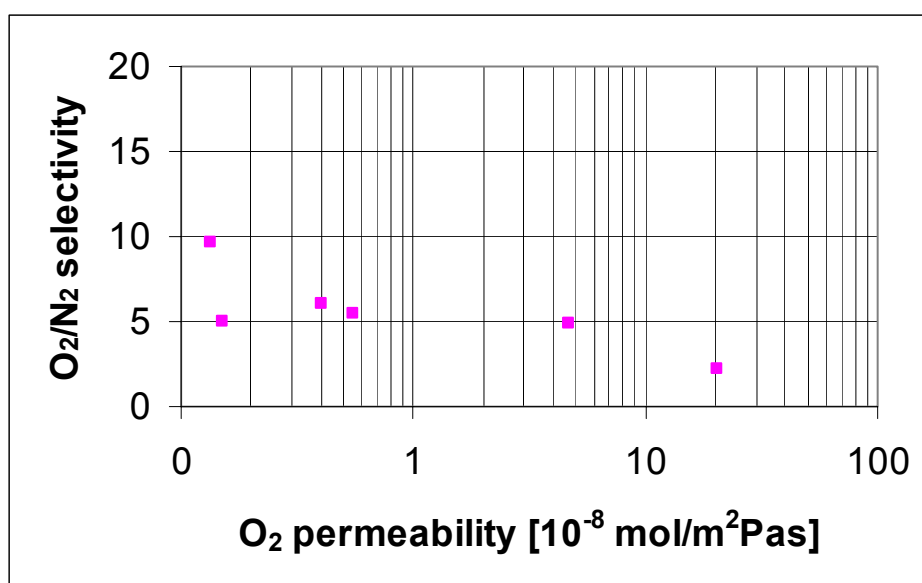

Figure 2.12   Selectivity-permeability relationship for commercially available membranes for oxygen production.

O$_2$/N$_2$-selectivity for commercially available membranes is typically around 5. These values are good enough to produce high concentration nitrogen from air for use as blanketing gas. The selectivity insufficient to produce a pure oxygen stream from air and as a result the use of polymeric membranes in denitrogenation processes is impractical, as only oxygen enriched air will be produced. There could be some potential in using membranes for oxygen enrichment in combustion processes. TNO is developing the HICLON process which aims the use of oxygen enriched air for the combustion process, produced e.g. by membrane technology.
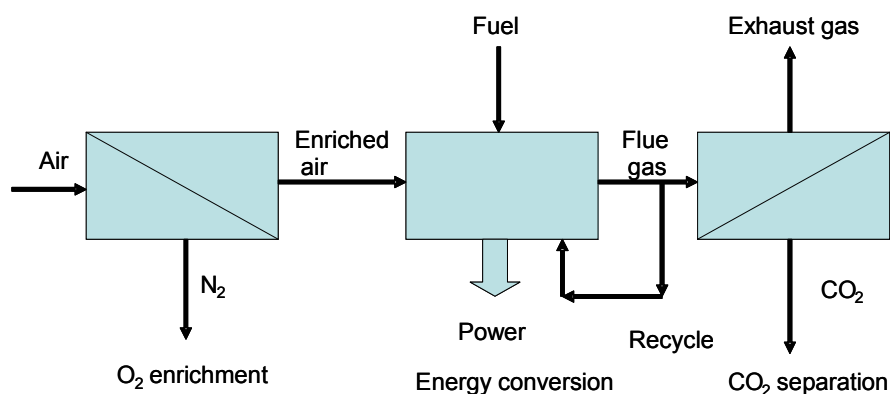

Figure 2.13   HICLON process flow sheet.

As a result of the higher oxygen content in the carbon dioxide content of the flue gas will also be higher. Also as a flue gas recycle is necessary to control the combustion temperature, the CO$_2$-content will be increased even further. The high CO$_2$-content in the flue gas will also facilitate the CO$_2$-separation. As such HICLON must be regarded as a hybrid between oxy-fuel combustion and post combustion capture. The concept is shown in Figure 2.13.

2.4   Chemical-looping combustion (CLC)

Chemical-looping combustion (CLC) is a combustion technology with inherent separation of CO$_2$, originally proposed by Richter en Knoche [3] and significant further development by Ishida and Jin [4]. The technique involves the oxidation of metals with air in an air (oxidation) reactor and the subsequent reduction of the formed metal-oxide with hydrocarbons in the fuel (regeneration) reactor. The metal is used as a contactor between fuel and air inhibiting the dilution of formed CO$_2$ with nitrogen. The fuel is introduced into the fuel reactor in gaseous form reacting with the oxygen caring metal:

$$((2n+m)M_yO_x + C_nH_{2m} \rightarrow (2n+m)M_yO_{x-1} + mH_2O + nCO_2 \quad (1)$$
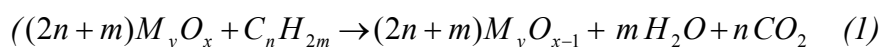
CO$_2$ and H$_2$O are the predominant flue gas constituents witch means that pure CO$_2$ can be obtained through condensation of the H$_2$O. The fuel reaction is in most

cases lightly endothermic. Regenerated metal is oxidized by air in a strongly exothermic reaction according to:

$$M_y O_{x-1} + \tfrac{1}{2}\, O_2 \rightarrow M_y O_x \qquad\qquad (2)$$

The metals Cu, Co, Ni, Fe and Mn possess oxides witch are suitable as oxygen carrier in a CLC system with natural gas as a fuel. From studies [7-8] it was found that the metals with the greatest potential for use in high temperature (1200 °C) CLC processes as preferred for power plant cycles are iron and nickel based compounds. This is because these metals can be oxidized and reduced without significant particle degradation or agglomeration in addition to good kinetics and high fuel gas conversion in the required reaction temperature range of the CLC power plant process.

The process investigated by several researchers is composed of two interconnected fluidized beds with active transport of metal particles in between them (Figure 2.14). Basically the process uses intermediate metal particles as the transport medium for oxygen separated from air to oxidize a gaseous fuel. As such it is a conversion process creating a stream of almost pure CO_2 and in oxygen depleted air without major pollutants. The intermediates used in the interconnected fluidized bed CLC studies are often Fe_2O_3 and NiO on support material [10-11]. The support is used to improve the mechanical strength of the particles but also to create a porous particle with a big active metal surface with minimal use of metal. Particles are made by extruding or freeze-granulation of a mixture of metal oxides, support material and some times pore forming agents, followed by drying or freeze-draying and finally sintering of the particles at 1300 °C in an oven [7-8].

One of the fluidized beds is the Air-reactor where metal particles are oxidized to metal oxide according reaction 2. The second fluidized bed, the Fuel-reactor is used to reduce the oxidized particles back to metal according reaction 1.
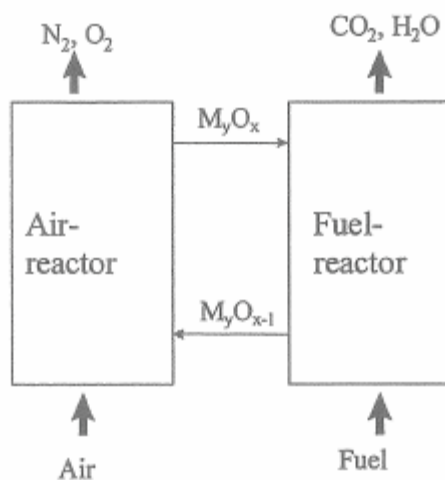

Figure 2.14   Basic flow sheet Chemical-looping Combustion [9].

In the interconnected fluidized bed CLC process (Figure 2.15) the oxidation reactor (1) is working as a circulating fluidized bed meaning that this reactor has the secondary function of active transport of the particles. Particles transported to the top of the air reactor are separated from the air stream with the help of a cyclone (2). The separated particles are transported through a gas tight seal made of particles and with the help of gravity dropped in the second fuel reactor (3). The "particle seal" ensures that the gas streams flowing through both fluidized beds are kept separated. Particles dropped into the fluidized fuel reactor are regenerated with help of a gaseous fuel.
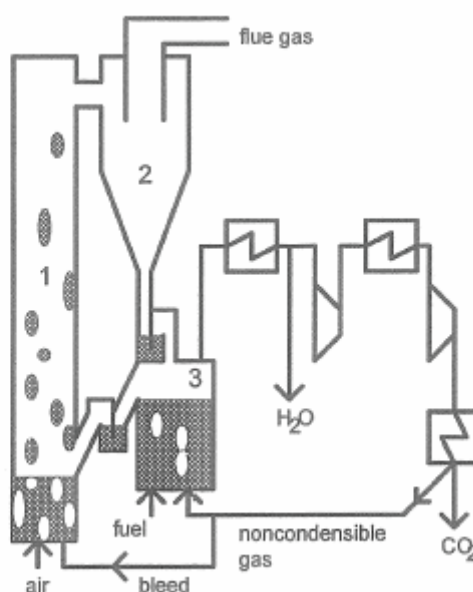
Figure 2.15   Process concept interconnected fluidized bed CLC process [9].

The mass flow of metal particles through the system is kept constant by removing as much particles from the fuel reactor as transported in. Particles are transported with help of gravity from the fuel reactor to the air reactor through a "particle seal" ensuring that the gases in the subsequent reactors stay separated.

The size of the CLC particles is governed by the need for sufficient reactivity and conversion, good transport properties in the circulating fluidized bed air reactor and good separation characteristics in the cyclone. These requirements are sometimes conflicting i.e. good reactivity and conversion demands very small particles while for operating the cyclone bigger particles are preferred. Typical sizes for CLC particles are 125-180 μm [8].

2.4.1 Chemical-looping combustion in a combined cycle power plant

Until recently the main research in chemical looping combustion was on Circulating Fluidized Beds (CFB) systems utilising gaseous fuels. Based on current development status a ZEPP would use an indirect heating-Rankine Cycle based, which is limited in thermodynamic cycle efficiency. Although CLC as such is an efficient conversion process, the CLC-CFB ZEPP would exhibit low (thermal to) electric efficiency compared to a natural gas fired combined cycle power plant. Hence this concept would not be more efficient then other "clean fossil concepts". Therefore the development of chemical looping combustion process targeted at the integration of CLC into a combined cycle power plant has become important. The novel part of this concept is the design of and the technical integration of the CLC reactor with a gas turbine. The result of this integration is a gas turbine where the burners are substituted by a reactor using metal particles (Figure 2.16). Like a conventional gas turbine the integrated CLC reactor/gas turbine concepts work at elevated pressure (17-20 bars). The oxidizing air flow is conceived by a fan that's driven by a turbine which in turn is driven by the expanding high temperature gases from the oxidation step. Excess power is transferred to a gearbox which drives an electric generator. The resulting in oxygen depleted hot air is passed on to a steam cycle after which it is vented to the atmosphere. The flue gas from the natural gas reduction cycle contributes to the steam cycle, but potentially this flue gas mixture could also be used for the direct generation of electric power through a turbine.
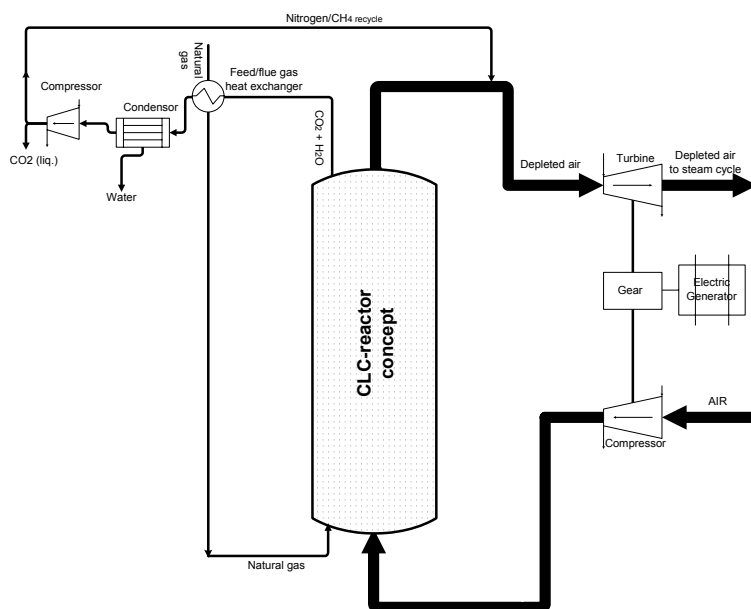

Figure 2.16   General process scheme CLC and combined cycle.

This depends on the availability of CO_2 tolerant high temperature steam turbines or gas turbines able to work with CO_2/H_2O, which are presently not available. The

natural gas feed is preheated with hot flue gas in the feed/flue gas heat exchanger. After passing through the feed/flue gas heat exchanger water is separated from the flue gas through condensation. The resulting almost pure CO_2 is condensed to the liquid state in a compressor with intermediate heat exchange. Because the reactor is already operated at elevated pressure, compression of CO_2 is relatively easy and cheap. Non-condensable like some N_2 slip and unreacted natural gas are recycled to the turbine where the unreacted natural gas will burn. The expected overall CO_2 separation efficiency of the proposed membrane chemical-looping reactor concepts will be 95-97% using nickel CLC-particles.

Integrated CLC reactor/gas turbine system are theoretical capable of achieving high CO_2 separation efficiencies with a relatively small penalty in plant thermal to electric efficiency compared to a gas turbine power plants. The major efficiency drop in this system is caused by the pressure drop in the reactor plus gas clean-up, in addition to the lower then optimal reactor outlet temperature for a turbine power cycle.

A practical problem facing integration of the interconnecting fluidised bed CLC systems with a gas turbine is the entrapment of small CLC particles in the hot expanding combustion gases. Particles entering the turbine lead to substantial damage of turbine blades resulting in huge repair costs or low turbine life span. Because of this an extensive gas cleanup is required which results in a higher pressure drop and more complex equipment. Furthermore the working temperature of the interconnecting fluidised bed CLC system is limited because of problems with particle ware in the fluidized beds. At present the practically feasible working temperature is significant less then the normal operating temperature of a gas turbine resulting in a relative low (51-52%) efficiency for an integrated CLC/gas turbine system. However the thermal to electric efficiency of the CLC CFB/gas turbine cycle can be raised to approximately the level of a standard gas turbine by raising the turbine inlet temperature through burning a small amount of fuel after the reactor. This burning of a fossil fuel results in the formation of CO_2 into the depleted air stream and by doing so lowering the CO_2 separation efficiency. However this is only a relatively small price to pay, as the expected overall CO_2 separation efficiency will still be around 80-85%.

2.4.2   New developments in CLC (packed beds and monoliths)

Current CLC developments are based on two interconnected fluidised beds (CFB), one for the oxidation of metal particles by air and one for the regeneration of particles by gaseous fuel [5]. Fluidized beds are well-described, widely used and attractive for its excellent heat transfer characteristics. However, to get the best efficiency out of CLC CFB integration with a combined cycle has to be made. Integration of CFB reactors into a combined cycle results in a higher pressure drop

and carryover of small particles, both are not advantageous properties in a combined cycle reducing efficiency and causing extensive wear to the hardware.

Until recently there has been little attention for the possible use of alternative and novel reactor concepts. Simplified the overall CLC process can be looked upon as an adsorption process in which the particles are regenerated by a fuel, resulting in desorption of reaction products. Adsorption processes for gas separation are often based on fixed particle beds or monoliths. Reasoning along the line of adsorption TNO and IFP recently started work on fixed bed and monolithic CLC reactor concepts. TNO started their approach using their knowledge of high temperature membrane reactors and absorption/adsorption technology. IFP is developing their novel CLC reactor using their knowledge on catalytic combustion and high temperature catalytic processes using monoliths.

The TNO membrane reactor concept:
The new CLC reactor concept under development by TNO combines a fixed bed reactor compromising of CLC particles with membranes in a concept called a CLC membrane reactor (see Figure 2.17).
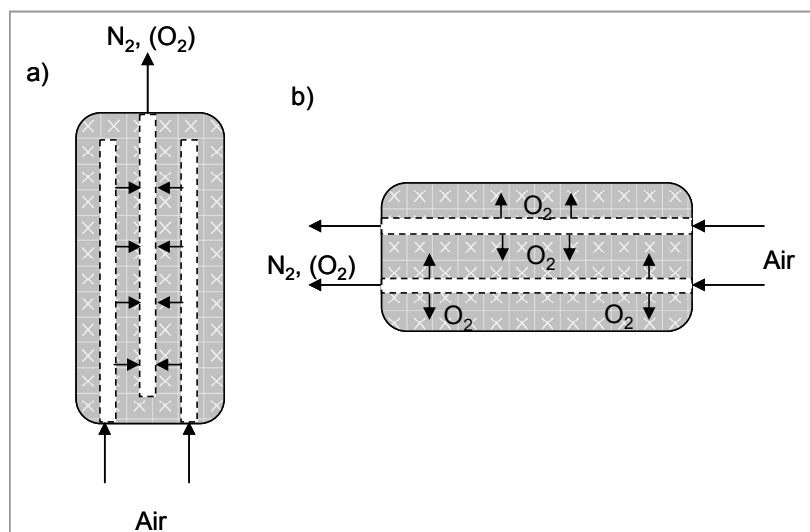
Figure 2.17   Packed Bed Membrane Reactors (a) convective and b) diffusive).

A major benefit of the CLC membrane assisted reactor is the physical separation between particles and the oxygen depleted product gas, which is fed to the gas turbine. The membranes form a physical barrier and hence particles will not be transported with the product gas streams, thus avoiding the risk of damage to the gas turbines as a result of particle carry-over. The use of membranes provides the opportunity of distributing and/or extracting gases at any point in the reactor. This enables an improved thermal control in a packed bed which is particularly relevant in the CLC oxidation reactor. Furthermore membrane reactors are in general more compact then fluidised bed reactors, particularly hollow fibre/tube reactors tend to be small in size, this is expected to lead to more compact and less costly equipment.

The membranes envisaged in the TNO concept are porous, i.e. without any significant selectivity, as they serve only to distribute the feed gas over the packed bed and retain the particles out of the gas stream to the gas turbine. Multiple reactors working in oxidation and reduction mode are needed to create a "simulated" continuous system. Smooth control of gas streams when switching between several reactors is needed. Important issues to be tackled are the use of high temperature control valves and the pressure drop over the bed, which limits the bed heights in case of small particles (< 1 mm). Being a "relative" of the CLC/gas turbine family of concepts the major benefits and drawbacks of this concept in principle also apply to the proposed membrane chemical-looping reactor concepts. However it is expected that the pressure drop in this novel reactor concept can be lowered compared to the "normal" interconnected fluidized bed system by reducing the effective bed height and improving the particle gas separation with the help of membranes. The process is being designed to minimize the use of high temperature control valves. A patent is filled for this TNO development [32].

The IFP Monolithic reactor concept:
The IFP concept combines the large available surface area of a monolith with CLC by coating a monolith with metal. The monolith is part of rotating wheel where the monolith is partly in contact with the oxidizing stream and partly in contact with the reducing stream, while the rest of the monolith is transiting through a sealing wall from one phase to the other. The IFP CLC reactor concept has the expected advantage of lower pressure drop and compacter equipment compared to the CLC interconnecting fluidised bed concept. Less favourable are the more problematic temperature control over the monolith and the dynamic sealing between de oxidising en reducing sites of the reactor.

In conclusion it can be said that both new CLC reactor concepts are interesting developments expected to exhibit a lower pressure drop, significant less carry-over of particles and more compact equipment compared to the CLC interconnecting fluidising bed reactor. However both new concepts are expected to be more difficult to control and to be more sensible to overheating.

2.4.3   New developments in CLC (Solid fuels and non-metallic particles)

Current state of the art circulating fluidized bed power plant employs steam cycles which do not render the most efficient power plant when using gaseous fuels. However regeneration with gaseous fuels is relatively easy and straight forward in a CFB and therefore chosen during the development of the chemical looping combustion. CFB is a proven technology which is efficiently employed for the combustion of solid fuels like Coal, pet-coke and biomass. The latest developments in advanced materials allow the use of supercritical steam cycles which has resulted in a considerable efficiency improvements compared to the older

generation CFB power plants, only to be matched by Integrated Gasification
Combined Cycle power plants, which is however far from a mature technology.
Difficulties with CLC CFB regarding temperature profile, pressure drop and
particle spill over make CLC CFB less suitable for gas turbine based cycles,
however these difficulties are not so relevant in a steam cycles.

The development of CLC CFB technology for solid fuels is therefore a logical step.
In Europe the main research on solid fuel CLC CFB is performed by Chalmers
University in cooperation with ALSTOM in the EU-funded project ENCAP. The
research on solid fuel CLC CFB focuses on the regeneration of the particles with
the solid fuel. The other parts of the process are unaltered to the gaseous fuel
operated system. The regeneration reactor in the solid fuel CLC CFB doubles as a
gasification and reduction reactor. The bed of the regeneration reactor is kept
fluidized by circulating a portion of the flue gas over the reactor. Ashes remaining
after the gasification of the solid fuel are transferred together with the intermediate
particles to the oxidation reactor. It is expected that ash particles are blown out of
the oxidation reactor because of their small dimensions, making some additional
measures to separate these fine ash particles from the flue gas necessary. Although
it is believed that the separation of ash particles from the flue gas can be achieved
with conventional equipment. However it remains to be seen if the separation of
ash from the reactors is as simple and straight forward as expected. Possible
problems with ash are sintered to the particles resulting in high wear of particles.
Furthermore it is likely that char is transferred from the regeneration reactor to the
oxidation reactor leading to a CO_2 slip. An additional uncertainty is possible slip of
unconverted fuel to the CO_2 product stream most likely in the form of CO.

In a $4 million US-DOE sponsored project ALSTOM in cooperation with Parsons
Energy & Chemical Group, ABB Lummus Global and PEMM Corporation ran
(9/30/03 - 9/30/05) an US-research program aimed at converting solid fuels in a
CLC CFB based power plant. The technology employed is however quite different
to the technology under development in EU-project ENCAP. The major difference
is that the USA process not employs a cycle based on oxidation/reduction of metal
atoms but rather a cycle based on oxidation/reduction of non-metalic atoms like
sulphur and carbon.

*Figure 2.18   The advanced chemical looping process under development in the USA
(Source ALSTOM).*

The process uses a sort of double chemical looping cycle with intermediate heat
transfer using bauxite (Figure 2.18). Calcium compounds are used to carry oxygen
and heat between the various reaction loops. In the first chemical loop CaS is
oxidized to $CaSO_4$ releasing heat to an intermediate heat transfer medium (bauxite)
and for use in the reduction reactor. In the reduction reactor the conversion of
$CaSO_4$ to CaS is used to gasify the coal into CO. This CO is converted in a steam
reformer to hydrogen and carbon dioxide. The carbon dioxide is then removed
from the gas using another chemical loop based on CaO & $CaCO_3$, where the heat
transferred by bauxite loop drives off the carbon dioxide.

ALSTOM claims that the US-process approach called hybrid combustion-
gasification chemical looping coal power technology has the potential to achieve
near-zero CO_2 emissions, exceed all current environmental regulations, meet or
beat IGCC efficiency, and cost less than $800 per kilowatt without CO_2 capture
and less than $1000 per kilowatt including CO_2 capture. These claims are however
difficult to verify as the studies these claims seem to be based on are not public.

Comparing the US to the EU process approach one can say that calcium sulphate is
probably less reactive then metal particles but is very cheap and a well known
substance in CFB technology. However the US-process scheme is much more
complex compared to the process researched in the EU-project ENCAP. The use of
an intermediate heating medium based on bauxite combined with the complex
process scheme creates the potential for large heat losses between process steps
leading to a low efficient process. Only with very good heat integration large heat
losses can be prevented. Furthermore it is known that cycles based $CaO/CaCO_3$ are
energy intensive because of the high calcination temperatures needed to release the

CO_2 and that the reactivity of CaO for the sorption of CO_2 decreases rapidly after only a few cycles.

Concluding can be said that the European approach looks the most promising rendering most likely a more compact, less costly and less complex plant when compared to the US-process. The US-process has the benefit of using much cheaper and more environmental friendly intermediate particles but they are probably less reactive then metallic particles. Because of the more complex process scheme it is likely that the US-process has larger heat losses resulting in a less efficient process compared to the European approach.

3. Comparison between concepts

Several options for oxy-fuel combustion are being researched for application in a Zero Emission Power Plant, each with their own benefits. However for a good evaluation of the oxy-fuel concepts it is better to make a broader evaluation and also compare the concepts against the best options in pre-combustion and post-combustion capture. These concepts can be qualitatively compared only because many are still in the first phase of development. Table 3.1 and Figure 3.1 show a comparison of concepts.

Table 3.1   Advanced Zero Emission Power Plants concepts (Source SINTEF).

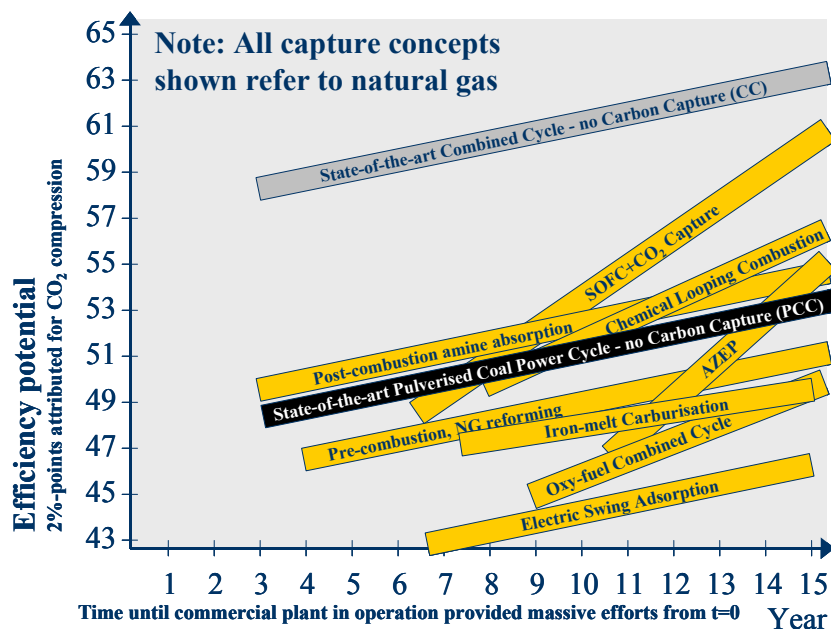| Technology	Energy loss [1]	CO_2 Capture	NO_x level
CO_2 Post-combustion capture	8-9%	85%-95%	< 25 ppm [2]
Fuel decarbonisation	11-12%	85%-95%	> 25 ppm
Oxy-fuel combustion	12-16%	100%	< 1 ppm
Chemical Looping combustion	7-10%	90%-95%	> 25 ppm
SOFC + CO_2 capture	2-10%	100%	<< 1 ppm
AZEP	7-13%	100%	<< 1 ppm
SOFC +GT + CO_2 capture	-(9-10%)	85%	<< 1 ppm

Figure 3.1   The expected efficiency potential against time to commercial implementation as Zero Emission Power Plants (Source SINTEF, 2004).

---

[1]   The lower figure is the expected theoretical optimum after full development.

[2]   Standard gas turbine NO_x emissions are around 25 ppm, in case of post-combustion using advanced multiple absorption liquids targeted at different species like NO_x, SO_x and CO_2 levels can be very low.
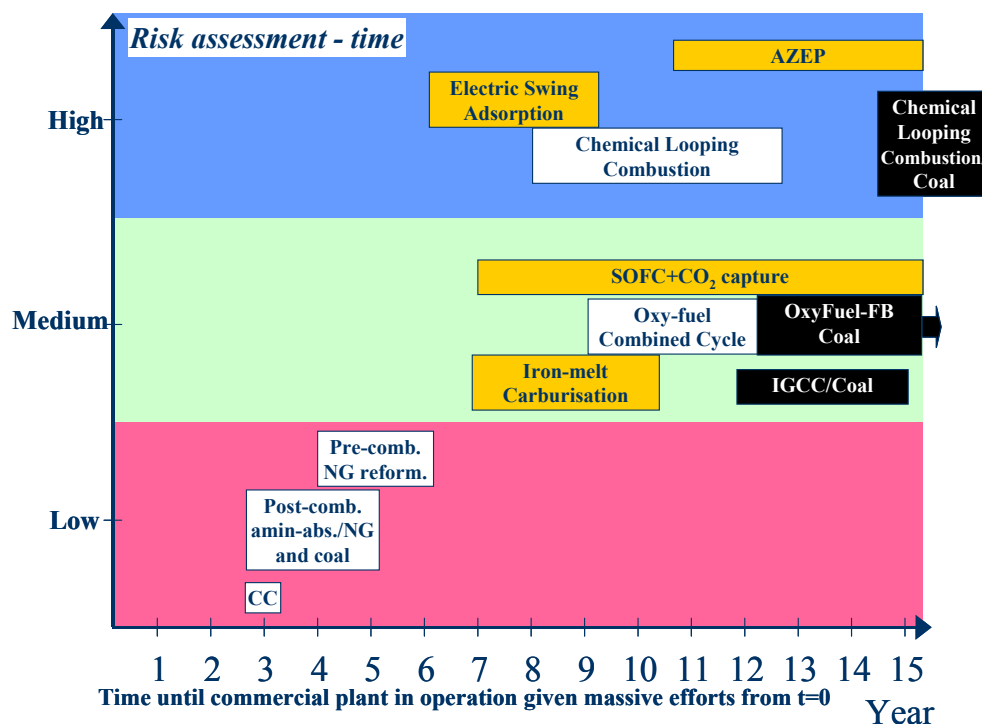
Figure 3.2   *The expected development risk[1] against time to commercial implementation*
                as Zero Emission Power Plants (Source: SINTEF, 2004).

Considering Table 3.1 adding development risk (Figure 3.2) and time (Figure 3.1)
to the equations one can only conclude that oxy-fuel combustion is by no means
superior to post-combustion capture on the short term as a ZEPP. Post-combustion
capture of SO_x is already well established and known by the energy sector. The
proven availability and reliability of flue-gas scrubbing equipment combined with
new developments in improved absorption liquids and possible integration of CO_2
or even NO_x capture with SO_x capture makes post-combustion capture the
technology to beat in the near future. Furthermore post-combustion capture can
also be easily integrated with coal fired power plants.

For the some what longer timeframe SOFC, Chemical Looping Combustion and
AZEP may become the preferred baseline technology for a ZEPP. There is
however serious doubt if it will be economically or even possible to generate the
large amount of power needed with SOFC. Also the development of oxygen
transfer membranes seems not as forthcoming as predicted. Stability and absolute
flawless operation of the membranes during long operation is still not guaranteed.
Furthermore AZEP and SOFC are relaying on gaseous fuels which are much more
limited then solid fuels like coal. In order to operate these technologies with solid

---

[1]   Low – i.e. technology that is almost commercially available, but not tested
       Medium - requires substantial efforts, but excludes barriers beyond reach and beyond
       current knowledge
       High - requires tremendous efforts and may need a new technology paradigm

fuels on has to gasify first these solid fuels resulting in higher plant costs and a sharp reduction in process efficiency. This makes CLC the most likely oxy-fuel technology to be competing against post-combustion for application in a ZEPP. Especially the new processes based on CLC look promising candidates.

4.   Internal oxy-fuel demo projects - developments

EU- Vattenfall
Vattenfall announced on the ENCAP general assembly 2005 their intention to build
in the near future (start project 2006-2008) a large scale demo Coal/lignite fuelled
ZEPP based on oxy-fuel combustion. The plant would use cryogenic produced
oxygen and combustion temperature moderation by flue gas recycling; Figure 2.3
depicts the most likely process scheme to be chosen for the Vattenfall large scale
demo. At the first International oxy-fuel combustion network meeting, held 28-29
November 2005 in Cottbus Germany, organised by the IAE Vattenfall confirmed
their intention for building the oxy-fuel demo plant. The large scale demo is planed
next to Vatenfall "Schwarze Pumpe" lignite fuelled power plant side. Design of the
30 MW_{th} demo started second half of 2005 after the board of Vattenfall agreed
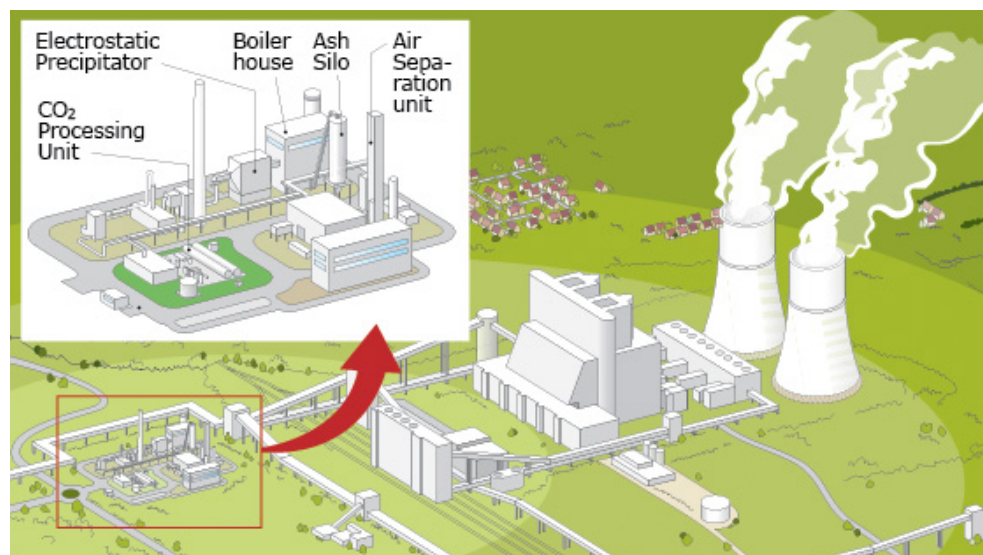May 2005 on the project € 50 million.

*Figure 4.1   Drawing of proposed oxy-fuel combustion pilot plant at the Schwarze Pumpe
power plant of Vattenfall (Source: Vattenfall [34]).*

The design attempts to use as much as possible commercial available components
while operating costs are kept down by using utilities and services from the near by
the Schwarze Pumpe power plant. In addition to the validation of the oxy-fuel plant
the project aims also at validation on shore CO_2 sequestration by storing the
captured CO_2 into underground "near" empty gas reservoirs under Berlin. Building
of the demo plant is expected to start early 2007.

US-CES [26]
CES proved the gas generator concept in 2000 by running a 110 kW pilot at the
University of California Davis. A 20 MW thermal gas generator was successfully
operated with over hundred starts and durations of up to three minutes in early

2003. Current development focuses on a small scale (up to 5 MW electrical) ZEPP based on a conventional indirect heating steam cycle. This project is executed with the participation of the California Energy Commission, NETL, Mirant and Air Liquide and started delivery of power to the grid in March 2005.

In addition to the work done on the Demo plant CES was awarded a DOE sponsored project aimed at further development on the CES technology for application on an syngas (from coal) fired variant. Parallel to this study DOE awarded Siemens a $14.5 million 56 month study on integrating a turbine suitable for the CES-cycle in order to produce a near zero-emission power plant. The turbine development work aims at combining gas and steam turbine components.

Joint Australian - Japanese project [35]
At the first International oxy-fuel combustion network meeting held 28-29 November 2005 in Cottbus Germany organised by the IAE a joined Australian-Japanese project was announced. The project is an evolution of the already longstanding cooperation of Japan and Australia in advanced power generation technologies. Important project partners are IHI of Japan and CS energy of Australia, with support of Australian and Japanese research institutes and universities. The project covers the conversion of one block of the old Callide A "relatively small[1]" coal fired power plant in Australia into a "near full scale[2]" demo according the process scheme Figure 2.3. The Australian/Japanese demo is with it 30 MWe bigger then the EU demo of Vattenfall. Important differences between the EU and Australian/Japanese project is that the EU project is base on a new build plant and is therefore expected to incorporate some of the advances and measures needed to built an optimized coal fired oxy-fuel power plant e.g. compacter equipment, better sealing of the boiler to prevent air in leakage and optimized flue gas recycling. The Australian – Japanese project has however a head start being based on an existing power plant, while proving the feasibility en retrofit ability of the oxy-fuel technology and by doing so both the EU and Australian –Japanese demo plants compliment each other.

---

[1]   Callide A build in 1965-69, is a 4x 30 MWe coal fired power station which is
       small compared to state of the art power plants recently build in EU.

[2]   This plant will be the larges oxy-fuel combustion demo in the world being in size
       80 – 100 MWt which is roughly the same order of magnitude of state of the art
       power plants in the EU.

5.   Conclusions

The main question for abatement of greenhouse gases is the extend we want to go in emission reductions and the cost we accept. The problem with oxy-fuel technologies is that they are very difficult to retrofit to current power plants. Oxy-fuel combustion therefore can only become dominant if very stringed abatement of nearly 100% is required and the huge cost of replacing current power plant technology with oxy-fuel is accepted. Some oxy-fuel technologies could in potential become more economically attractive compared to post-combustion capture. But only under the conditions that significant improvements in these oxy-fuel technologies are made and technological developments in post-combustion capture stagnate.

For the some what longer timeframe SOFC, Chemical Looping Combustion and AZEP may become the preferred baseline technology for a ZEPP. These technologies promise limited lower or even in case of SOFC + GT better power plant efficiency compared to near future state of the art power plants built according conventional design. There is however serious doubt if it will be economically or even technically possible to generate the large amount of power needed with SOFC. Also the development of oxygen transfer membranes seems not as forthcoming as predicted. Stability and absolute flawless operation of the membranes during long operation is still not guaranteed. Furthermore AZEP and SOFC relay on high quality gaseous fuels which are in much more limited supply then solid fuels like coal. In order to operate these technologies with solid fuels one has to gasify first these solid fuels resulting in higher plant costs and a sharp reduction in process efficiency. CLC has good potential for integrating gasification of solid fuels in the fuel reactor and could benefit from recent research in pressurised CFB boiler technology. CLC-CFB therefore is the most likely oxy-fuel technology to be competing against post-combustion for application in a solid fuelled ZEPP in the near future. The new processes based on CLC based on fixed bed concepts look promising candidates for a gaseous fuelled ZEPP and should therefore be further researched.

6. References

[1] Julbe A. et.al., "Porous ceramic membranes for catalytic reactors – overview and new ideas*", Journal of Membrane Science, 181(2001)3-20*

[2] Bredesen R., Jordal K., Bolland O., "High-temperature membranes in power generation with CO_2-capture", *Chemical Engineering and Processing, 43(2004)1129-1158*

[3] Richter H.J., Knoche K., "Reversibility of Combustion processes, Efficiency and Costing – Second Law Analysis of Processes", ACS Symposium series 235 (1983), 71-85

[4] Ishida M., Jin H., "A New Advanced Power-Generation System Using Chemical-Looping Combustion", *Energy, 19(4) (1994), 415–422*

[5] Lyngfelt A., Leckner B., Mattisson T.,"A fluidised-bed combustion process with inherent CO_2-separation; application of chemical-looping combustion", *Chemical Engineering Science, 56(2001)3101-3113*

[6] Sint Annaland van M., "*A novel reverse flow reactor coupling endothermic and exothermic reactions*", Twente University, 2000

[7] Adánez J., Diego de L.F., García-Labiano F., Gayán P., Abad A., "Selection of Oxygen Carriers for Chemical-Looping Combustion*", Energy & Fuels 18 (2004)371-377*

[8] Cho P., Mattisson T., Lyngfelt A., "Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion", *Fuel 83(2004)1215-1225*

[9] Mattisson T., Järdnäs J., Lyngfelt A., "Reactivity of Some Metal Oxides Supported on Alumina with Alternating Methane and Oxygen-Application for Chemical-Looping Combustion", *Energy & Fuels 17(2003)643-651*

[10] Ishida M., Jin H., Okamoto T., "A Fundamental Study of a New Kind of Medium Material for Chemical-Looping Combustion ", *Energy & Fuel 10(1996)958-963*

[11] Mattisson T., Lyngfelt A., Cho P., "The use of iron oxides as an oxygen carrier in chemical-looping combustion of methane with inherent separation of CO_2 ", *Fuel 80(2001)1953-1962*

[12] www.alstom.com

[13] O. Marin et al., "*High efficiency, zero emission power generation based on a high temperature steam cycle*", Air Liquide, USA

[14] Website Clean Energy Systems, http://www.cleanenergysystems.com

[15] Ola Maurstad (SINTEF), *EMINENT Workshop on New Energy Technologies*, Latvia, 2004

[16] Website van IEA Greenhouse Gas R&D program, www.ieagreen.org.uk

[17] Website Chalmers University, chemical looping, http://www.entek.chalmers.se/%7Eanly/co2/co2clc.pdf

[18] Sven Gunnar Sundkvist, ALSTOM Power Sweden AB, Timothy Griffin, ALSTOM Power Technology Ltd, Switzerland, Niels Peter Thorshaug, Norsk Hydro ASA, Norway, "*AZEP - Development of an Integrated Air Separation Membrane - Gas Turbine*", http://www.vok.lth.se/azep/concept.htm

[19] Olav Bolland (NTNU), Hanne M. Kvamsdal (SINTEF Energy Research), John C. Boden (BP Oil International), "*A Thermodynamic Comparison of the Oxy-fuel Power Cycles Water-cycle, Graz-cycle and Matiant-cycle*", International Conference on Power Generation and Sustainable Development, Liège (Belgium), 8/9-10-2001

[20] Terry Wall, Chanddong Sheng, Raj Gupta, Chemical Engineering, University of Newcastle, Australia, "*Oxyfuel combustion for sequestration ready CO_2 – Technology status, assessment and research needs*". 14th IFRF Members Conference, Noordwijkerhout, 2004

[21] Bouwmeester, H. J. M.; Van Der Haar, L. M. "Oxygen permeation through mixed-conducting perovskite oxide membranes", *Ceramic Transactions ,127 (2002), 49-57*

[22] Wilkinson M.B., Boden J.C., Gilmartin T., Ward C., Cross D.A., Allam R.J., Ivens N.W., "*CO_2 capture from oil refinery process heaters through oxyfuel combustion*", Proceedings of 6th International Conference on Greenhouse Gas Control Technologies, 2002, Elsevier publishers.

[23] Naskala, N.ya, (Alstom) *Presentation Clean Air Lissabon*, 2005

[24] Website NETL: www.netl.doe.gov/publications/ factsheets/project/Proj293.pdf

[25] Boer de B., "*SOFC Anode (Hydrogen oxidation at porous nickel and nickel/yttria-stabilised zirconia cermet electrodes*", Twente University, 1998

[26] www.cleanenergysystems.com

[27] Kohl A.L., Nielsen R.B.; "Gas Purification", 1997, Gulf Publishing Company

[28] Kvamsdal H., Maurstad O., Jordal K., Bolland O.; "Benchmarking of gas-turbine cycles with CO_2 capture" Proceedings of 7th International Conference on Greenhouse Gas Control Technologies, 2004, Elsevier Science Volume 1 (2005) 233-242

[29] Maurstad O., Bredesen R., Bolland O., Kvamsdal H.; "SOFC and Gas Turbine power systems- Evaluation of configurations for CO_2 capture" Proceedings of 7th International Conference on Greenhouse Gas Control Technologies, 2004, Elsevier Science Volume 1 (2005) 273-281

[30] Jansen D., Dijkstra J.W.; "CO_2 capture in SOFC-GT systems", second annual conference on CO_2 sequestration, 2003, Alexandria, Virginia, USA

[31] www.powergeneration.siemens.com/en/fuelcells/hybrid/index.cfm

[32] TNO patent application (05076166.7): "Method for regulating the heat and the CO_2 concentration of the air in an enclosed space"

[33] IPCC report "Carbon Dioxide Capture and Storage", 2005, Cambridge University Press

[34] www2.vattenfall.com

[35] www.co2captureandstorage.info/networks/oxyfuelinaguralworkshop.htm

7.   Authentication

Name and address of the principal:

CATO

p/a UCE

attn. E. Lysen

Heidelberglaan 2

3584 CS Utrecht

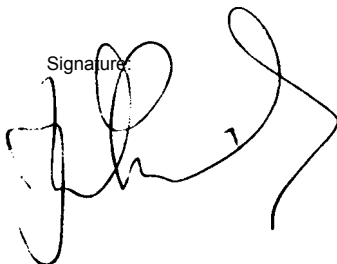Names and functions of the cooperators:

Dr. P.H.M. Feron   Project leader

N.A.M. ten Asbroek (M.Sc.)   Author

Names and establishments to which part of the research was put out to contract:

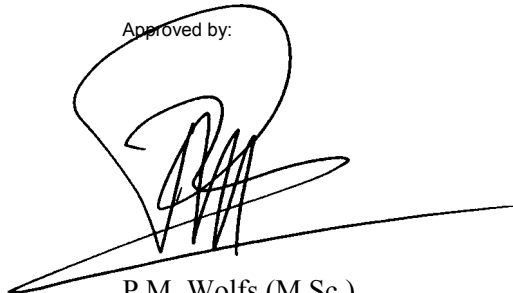Date upon which, or period in which, the research took place:

August 2006

Signature:

Approved by:

J.W. Assink (M.Sc.)   P.M. Wolfs (M.Sc.)

project manager   team manager