IMPROVED OXYGEN PRODUCTION TECHNOLOGIES

Technical Study

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IMPROVED OXYGEN PRODUCTION TECHNOLOGIES

Background

Large quantities of oxygen are required by some power generation and industrial processes with CO_2 capture, for example about 40,000 tonnes/day for a 2,000 MW coal fired oxy-combustion power plant and about 15,000 tonnes/day for the same size of IGCC plant with CO_2 capture. Oxygen production plants account for about 10% of the cost of an IGCC with CO_2 capture and 20% of the cost of a coal-based oxy-combustion plant. Oxygen production is therefore a key technology for CO_2 capture. Large oxygen plants currently use cryogenic air distillation, which has been practiced for over 100 years. Alternative technologies know as Ion Transport Membranes (ITM) or Oxygen Transport Membranes (OTM) are currently being developed.

Study Description

This report includes descriptions of cryogenic and membrane oxygen production processes, their components and their integration into power generation and synthesis gas production processes with CO_2 capture. Recent and potential future improvements in these oxygen production processes are discussed.

The report was written by a consultant, Rodney Allam, formerly of Air Products. The report does not include information from confidential sources.

Results and Discussion

Cryogenic oxygen production has been demonstrated in plants with capacities of up to 4,000 tonnes/day. 5,000-6,000 t/d single train plants are being offered commercially and machines for 10,000 t/d capacity plants could be built now with low risk, if there was a demand for CO_2 capture plants. Cryogenic oxygen production is an energy intensive process, for example producing 95% purity oxygen at a pressure of 1.6 bar requires about 200 kWh/tonne O_2 using current technology. This corresponds to almost 6 percentage points of efficiency for a coal-fired oxy-combustion power plant. Decreases in the energy consumption of cryogenic oxygen plants will come from the use of more efficient and complex process cycles, increased gas compressor efficiencies and improved process integration. The use of more complex cycles will become worthwhile because of the increased cost of electricity resulting from CO_2 capture. Larger single train plant sizes will reduce the specific capital cost of oxygen production.

Ion transport membranes, which are being developed by a number of companies, use dense mixed metallic oxides which are 100% selective for oxygen. They operate preferably at or above 800°C and the most convenient arrangement is to integrate them into a gas turbine. The resulting oxygen can be used for gasification or oxy-combustion. Studies indicate that ITM's could significantly reduce the net capital and power costs for oxygen production, for example by about 35% in IGCC. However, ITM's have not yet been demonstrated in large scale plants, so these savings are subject to uncertainties. Full size membrane modules with a capacity of 0.5t/d have been successfully tested. The next stage of development will require a high capacity automated production line capable of module production with consistently high performance and minimum cost. Long term performance, efficiency and reliability will need to be demonstrated. A multiple module unit to supply 2,000 t/d of O_2 could be included in the FutureGen plant.

Expert Reviewers' Comments

The draft study report was reviewed by various external experts. IEA GHG is grateful to those who contributed to this review. The report was generally well received by the reviewers. Most of the comments were editorial or requests for further information, which were taken into account as far as possible subject to limitations on the availability of information in the public domain.

Major Conclusions

The current developments in improved oxygen production techniques are expected to reduce significantly the costs of oxygen in plants with CO_2 capture. Cryogenic oxygen will still have a potential in the future for specific applications, particularly coal-fired oxy-combustion power plants.

Recommendations

IEA GHG should continue to monitor developments in oxygen production technologies and provide a short updated review at an appropriate time.

IMPROVED OXYGEN
PRODUCTION TECHNOLOGIES

REPORT TO
International Energy Agency
Greenhouse Gas R&D Programme
(IEA GHG)

RODNEY JOHN ALLAM

SUMMARY

Oxygen production is a major part of the energy consumption and capital cost of oxy-fuel combustion and fossil fuel gasification systems with CO_2 capture.

The current oxygen production process is the cryogenic separation of air by distillation, which is a mature technology having been practiced for over 100 years. Adsorption and membrane separation technologies are not economic for the extremely large oxygen production requirements of future oxygen based power plants, which could range up to 40,000 tonne/day, for a 2000 MW oxy-fuel coal fired unit.

A new process, which is still in the development phase, produces oxygen by diffusion through dense mixed oxide membranes at temperatures above 700°C. The oxygen molecules ionise and pass through the membrane when there is an oxygen pressure gradient, while electrons pass counter-currently through the positive ion matrix. These transport membranes have very large flux rates and infinite selectivity for oxygen. They offer up to 50% oxygen cost reduction potential, compared to the conventional cryogenic process. The need for a high temperature air source means that they must be closely integrated with the high temperature processes which use the oxygen produced, for economic application.

Oxygen requirements for large CO_2 capture systems vary from about 4.9 tonne/day per MW electrical capacity for a natural gas fired combined cycle system to 19.5 tonne/day per MW electrical capacity for a coal fired supercritical oxy-fuel boiler. The required oxygen purities are in the range 90% to 97% while, delivery pressures range from about 1.7 bar for an oxy-fuel coal fired boiler to 70 bar for current coal gasification systems and over 100 bar for oxy-fuel and gasification systems currently under development.

Cryogenic air separation plants currently range in size up to about 4000 tonne/day. CO_2 capture systems will require larger single train plant capacities which will involve larger distillation columns, heat exchangers and compressors but no radical changes in current technology. The second major change will be the need to use more efficient and complex process cycles for the air separation unit caused by the increase of about 40% in the cost of electricity with CO_2 capture. There is little scope for efficiency improvements in current plants by using large lower pressure drop equipment or by reducing the already very low temperature differences in heat exchangers. Most of the improvements will come from increased separation efficiency in the air distillation system with the use of heat integrated multiple distillation columns to replace the current Linde double column system, in increased gas compressor efficiencies and in improved process integration. Larger single train plant sizes will reduce the specific capital cost of oxygen production.

Integration of the cryogenic air separation plant with the power system leads to significant benefits in overall oxygen costs. The oxy-fuel coal fired boiler producing supercritical steam for a turbine can

utilise heat of compression for boiler feed-water and condensate pre-heating derived from the air separator using adiabatic compressors which also saves cooling water. The integrated gasification combined cycle power system can use air bled from the gas turbine compressor to provide part or even all of the air for the oxygen plant. Careful optimisation can maximise gas turbine performance. Nitrogen from the air separation plant is mixed with hydrogen fuel to minimise nitrogen oxide contamination of the gas turbine exhaust and maximise the gas turbine power output. The control of the integrated system must be carefully designed to allow ramping of the power output in response to changes in electrical demand. High ramp rates of oxygen production are possible with the assistance of a back-up liquid oxygen storage and vaporisation system.

Oxygen ion transport mixed oxide membrane technology is under development in a number of companies which are targeting high volume oxygen generation integrated with power and hydrogen production systems with possible CO_2 capture. The ion transport membrane (ITM) for pure oxygen production is best integrated with a gas turbine, where the hot adiabatically compressed air can be withdrawn from the air compressor discharge, further heated and used as feed to the ITM module. The diffusing low pressure oxygen is compressed, following heat recovery and used in the fossil fuel gasifier. The oxygen content of the non-permeate stream is still sufficiently high to provide for combustion in the gas turbine. Recommended operating conditions and guidance on the calculation of oxygen recovery in the ITM are presented. A parallel development of ITM systems is to use them to produce H_2 + CO synthesis gas by steam/natural gas reforming. The exothermic reaction of the diffusing oxygen with components such as CH_4, H_2, CO is balanced by the endothermic reforming reaction. The highly reducing conditions give an extremely low equilibrium partial pressure of oxygen on the permeate side and allow the ITM unit to function with near atmospheric pressure heated air on one side of the membrane and say 30 bar reforming on the permeate side. Each manufacturer's development programmes are presented and details of equipment, integrated process arrangement development targets and costs are presented as available.

The current developments in improved oxygen production techniques are encouraging and they should result in significant reductions in oxygen costs for CO_2 capture Cryogenic oxygen will still have a potential in the future for specific applications particularly coal-fired oxy-fuel power stations.

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1. INTRODUCTION

1.1 Background

The International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) was established in 1991 to evaluate technologies that could be used to avoid emissions of greenhouse gases, particularly from the use of fossil fuels. IEA GHG is an international organisation, supported by seventeen countries world-wide, the European Commission and several industrial organisations.

The main focus of IEA GHG's work has been on capture and storage of CO_2. Studies have been carried out to assess technologies for CO_2 capture, how they could be applied and how they compare to alternative greenhouse gas abatement options. Two of the main technologies for CO_2 capture are oxy-combustion and pre-combustion capture, which involves partial combustion (gasification) of a fuel, in many cases using oxygen. Oxygen production accounts for a major part of the energy consumption and cost of oxy-combustion and gasification processes. Reductions in the energy consumption and costs of oxygen production could therefore substantially reduce the costs of CO_2.capture.

1.2 Oxygen Production

The technology currently used for large scale oxygen production is cryogenic air separation. This is a mature technology with a well established cost base and a number of international groups able to supply any type of plant. It is difficult to obtain detailed costs and performance data on cryogenic air separation plants. The industry is highly competitive and data of this nature are generally regarded as confidential. Any performance comparisons that are made may be based on estimates described in patents and publications. The power requirements of compressors can be estimated from published pressure and temperature conditions existing in the systems described. Capital costs are much more difficult to establish. They will be highly site specific and they will depend on factors such as the degree of prefabrication of major sub assemblies. At present there is a world-wide escalation in the cost of major projects due to the sudden huge increase in material and labour costs which makes any historical cost data unreliable. Some significant improvements have been made, particularly increase in train sizes and in the development of cycles which have lower power consumption but more complex designs.

Their has been an important breakthrough in oxygen production technology with the development of mixed metallic oxide ceramic materials which have the property of diffusing pure oxygen at extremely high flux rates at high temperature. These materials are known as Ion transport

Membranes (ITM), and also as Oxygen Transport Membranes (OTM). They offer the possibility of a significant reduction in the cost of oxygen. The jump in operating conditions from cryogenic temperatures to very high temperatures means that a completely different set of optimum operating conditions for ITM must be used. The necessity to economically achieve the simultaneous high temperature with an oxygen partial pressure difference for diffusion means that the ITM systems must be optimally integrated with associated high temperature processes if they are to be used in future. These materials are at present still in the development stage. There performance and composition is now well established in small test cells and pilot plants. The ITM is a ceramic material which must be fabricated in a geometry which gives high surface area, low membrane thickness, a good geometry allowing a high specific area of membrane in a given volume, a long life at operating conditions, the ability to withstand thermal and pressure cycling, and good mechanical stability, The membrane modules must have robust ceramic to metallic transition pieces which are leak free and the modules must be located in a pressure vessel operating in high pressure high temperature conditions. It is this development of the large scale ITM units which is now in progress. The patent and published information on ITM systems gives a good indication of the likely performance compared to the traditional cryogenic process in applications for power and hydrogen production. Capital cost data is very sparse and at this stage cannot be relied on. All that can be said is that there will be significant savings in oxygen costs in specific applications.

The other two methods of air separation which are currently in use are the polymeric membranes operating at atmospheric temperatures and the use of solid zeolite materials in pressure swing multi-bed adsorber systems. Neither of these methods is suitable for the production of the very large quantities of oxygen required for oxygen based CO_2 capture technologies. The pressure and vacuum swing oxygen units are only economic at up to about 150 tonne/day capacity at purities of about 90% to 93%. The membrane systems are only used for small scale low purity nitrogen production.

Chemical looping is not covered in this report which focuses on the production of oxygen.

1.3 Scope of Work

This study will present the best current information on the potential for future improvements in oxygen production technologies. The study will describe technologies, identify technical development issues which need to be resolved, timescales for commercial availability and the likelihood of success and estimate the impacts on energy consumptions and costs. The study will concentrate on technologies for large plants such as electrical power plants and large scale H_2 plants as these are likely to be the main applications for CO_2.capture and storage but technologies which are better suited to smaller scale application will also be considered, in case future developments could affect the viability of CO_2.capture at smaller scales.

- Current technologies for oxygen production and ways in which they have improved in recent years will be reviewed. The two major technologies considered will be cryogenic air separation and the high temperature oxygen ion transport membranes. A brief overview of pressure swing adsorption and polymeric membrane systems for the production of smaller quantities of oxygen will be considered.

- Potential improvements in current oxygen production technologies will be identified and discussed.

- Particular challenges for oxygen production technologies in power plants and hydrogen plants with CCS such as safety considerations, reliability will be identified and discussed.

- The current state of development of ITM/OTM high temperature membrane systems will be reviewed and major development programmes will be described.

- Current and future methods of integrating ITM and cryogenic oxygen plants into coal and gas fired power generation and hydrogen plants with CO_2 capture will be reviewed.

- The challenge presented by the very large oxygen production requirements for typical power stations designed for carbon dioxide capture will be discussed.

- The impacts of future developments in oxygen production technologies on the performance and costs of power plants with CCS will be estimated, as far as possible, given the state of development and limits on availability of confidential information.

- The major technical development issues for improved oxygen production technologies will be identified and discussed. Timescales for possible commercial availability will be estimated.

2. CARBON DIOXIDE CAPTURE FROM FOSSIL FUELS

2.1 The Use of Fossil Fuels

Carbon dioxide (CO_2) is the major component of anthropogenic emissions to the atmosphere which are the probable cause of global temperature rise. The major source of anthropogenic CO_2 emission is the combustion of fossil fuels for the production of electrical energy, for heating purposes, for the production of chemicals and other materials where CO_2 is a by-product and from fuel used for transportation systems. Mankind must drastically reduce CO_2 emissions to avoid the risk of a catastrophic atmospheric temperature rise.

Fossil fuels currently make up about 86% of mankind's primary energy needs. The remaining `14% covers renewables, of which hydro-electricity is the major part, nuclear and biomass. Fossil fuels are likely to remain by far the largest source of primary-energy for the next 50 to 100 years particularly with the massive increase in world population and the rapid development of advanced high energy consuming economies in countries such as China and India. This is likely to significantly increase the consumption of fossil fuels in the next few decades in spite of efforts to introduce CO_2 free energy sources such as renewables or nuclear power.

A further challenge is the projected rapid rise in the total world fossil fuel market share for coal, which will be the primary energy source in three of the world's largest economies, China, India and USA. Carbon dioxide emissions from coal are far higher than from oil or natural gas combustion for a given power output or heating load. Our challenge will be to introduce CO_2 capture and CO_2 geological storage for the major CO_2 emission sources if the projected global atmospheric temperature rises and climate change is to be mitigated.

The IPCC special report on CO_2 capture and storage (REF. 1) records the global emission of CO_2 in the year 2000 at 23.5 Gt with nearly 60% of this total attributed to 7887 emission sources above 100,000 tonne/year of CO_2. Of this total, 4942 sources were from electrical power production which in total emitted 10.5 Gt of CO_2. The majority of these emissions are in flue gas streams containing less than 15% CO_2. The remaining 40% of global CO_2 emissions from small point sources are mainly from transportation emissions and for heating purposes. If mankind changes to hydrogen (H_2) fuels for vehicular transport in the future it will be possible to convert fossil fuels to H_2 in large centrally located plants with CO_2 capture from a relatively small number of point sources.

This concentration of CO_2 emissions into a manageable number of large point sources makes it possible to select CO_2 capture from fossil fuels as the main method we have for drastically cutting CO_2 emissions in the immediate future.

2.2 Classification of CO_2 Capture Processes

There are a few points of CO_2 emission from industrial sources at very high concentrations in excess of 95% which can be easily captured. Examples include ammonia and methanol production, oil and gas processing and petrochemicals. These CO_2 emission sources make up only about 2% of the world total. Most other sources of CO_2 emission are at concentrations below about 15%. Cement plants, which account for about 5% of global emissions, have concentrations of around 25%.

There are three main methods which can be applied to treat point sources of low CO_2 concentration at near atmospheric pressure to capture the CO_2 as a high pressure, high purity stream suitable for transportation to a storage location.

2.2.1 Post Combustion Capture

The CO_2 present in the flue gas from a fossil fuel combustion process with air is removed mainly by scrubbing with an aqueous amine solvent. No oxygen is used in this process.

2.2.2 Pre-Combustion Capture

This process converts the primary fossil fuel to hydrogen with conversion of the carbon content to CO_2 which is then separated from the hydrogen product stream. The hydrogen can then be used as the fuel gas in a gas turbine combined cycle power generation system or it could also, in the future, be used as a transportation fuel.

The most widely used process is steam/natural gas reforming where natural gas or light hydrocarbon feedstock's are catalytically reacted with steam to produce a hydrogen plus carbon monoxide (CO) mixture (syn-gas)

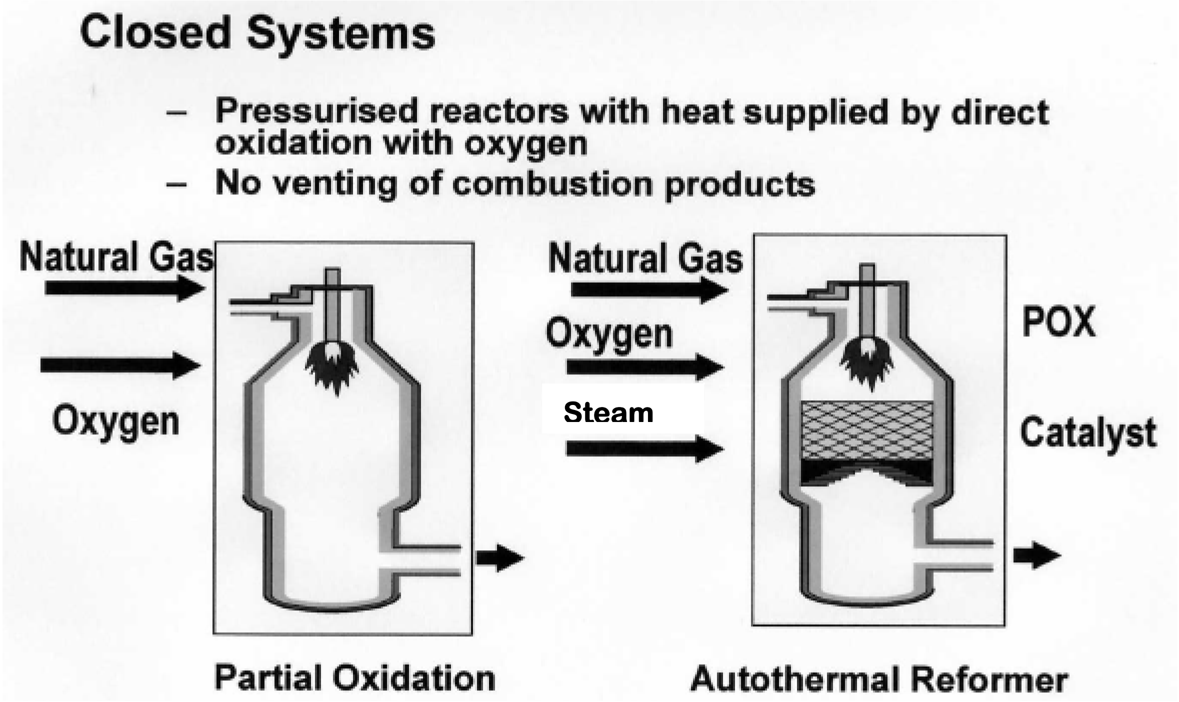
$$CH_4 + H_2O = CO + 3H_2$$

The reaction is endothermic and carried out typically at pressures of 20 bar to 35 bar and temperatures of 800^oC to 900^oC in a multi-tube furnace heated by a fuel gas stream. In a simultaneous reaction (the shift reaction) the CO reacts catalytically with steam to produce $H_2 + CO_2$.

$$CO + H_2O= H_2 + CO_2$$

The reaction products are H_2 and CO together with some CO_2 and excess steam. The gas mixture is cooled to produce excess steam and most of the remaining CO is catalytically converted with steam to CO_2 and H_2 at lower temperatures. CO_2 is generally removed from the high pressure gas mixture using an amine scrubbing process following cooling to condense excess water vapour. The system has the disadvantage of requiring about one third of the fossil fuel heat energy to be used for furnace heating which results in a maximum CO_2 recovery from the high pressure H_2 + CO_2 stream of about 60% of the CO_2 produced with the remaining CO_2 vented at low concentration.

The partial oxidation process (POX) (FIG. 1) uses the reaction between a hydrocarbon, such as methane, and oxygen to produce H_2+CO syn-gas at a temperature of at least $1300^{o}C$. There is also some complete oxidation to CO_2 and H_2O. Operating pressures of up to 100bar have been used. Oxygen pressure would be up to 110bar at a purity of 90% to 99.6% depending on the application.



Closed Systems

- Pressurised reactors with heat supplied by direct oxidation with oxygen
- No venting of combustion products

Fig 1

The auto-thermal process (ATR) (FIG. 1) combines a partial oxidation burner and a catalytic steam/hydrocarbon reforming reaction in a single reactor. All the CO_2 produced in the process can be removed easily from the high pressure H_2 stream following CO shift reaction. A natural gas stream mixed with steam is partially oxidised in a burner with a limited flow of oxygen such that the product gas temperature is above $1200^{o}C$ and there is still a significant fraction of methane present. The gas is then passed through a fixed catalyst bed in which steam/methane reforming takes place. Typical exit conditions are $1050^{o}C$ and 30 bar pressure. No external heating is required. Following shift conversion all the CO_2 produced from the natural gas feed can be recovered using an amine scrubbing unit. The ATR is the preferred process for large scale production of hydrogen from natural gas with CO_2 capture because of its low capital cost, its high CO_2 recovery from a high pressure gas stream and its high efficiency. Single stream units of very large capacity are being constructed to supply syn-gas for Fischer-Tropsch conversion to hydro-carbon liquids (REF. 2). The efficiency of the process can be increased by utilising the sensible heat in the high temperature ATR reactor product gas to provide heat for a convective steam/methane reformer which is arranged either in series or parallel with the ATR reactor. The ATR reactor requires an oxygen purity of 90% to 97% at a pressure of up to about 45 bar.

Heavier fuels such as coal, bitumen or petroleum coke must be converted to $H_2 + CO_2$ by a process of partial oxidation using pure oxygen followed by shift reaction. A typical coal with a carbon to hydrogen atomic ratio of about C : 0.4H would be partially oxidised to CO and H_2.

$$C\,H_{0.4} + 0.5O_2 \rightarrow CO + 0.2\,H_2$$

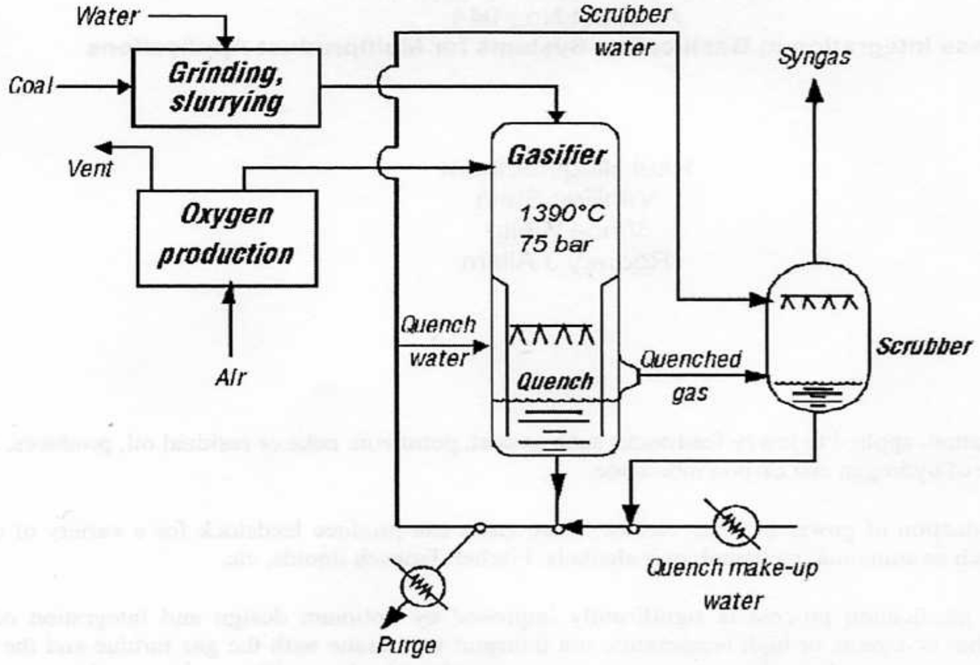
The partial oxidation process takes place for coal at a temperature in excess of 1400°C at pressures of 40 bar to 70 bar. The high temperature is required to minimise the proportion of unconverted carbon in the coal ash. Some of the coal is completely combusted to provide the necessary heat required.

$$C\,H_{0.4} + 1.1O_2 \rightarrow CO_2 + 0.2\,H_2O$$

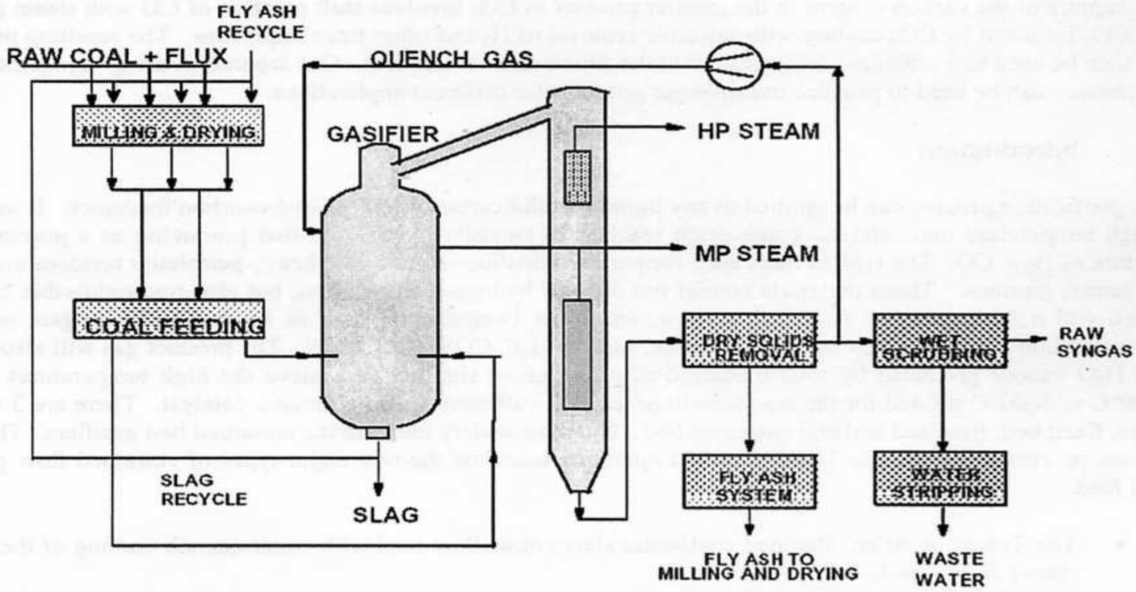
The shift reaction also occurs and converts some of the CO with steam to CO_2 and H_2.

The two major systems currently used for partial oxidation or gasification of heavy fuels are the Shell dry coal gasifier and the GE/Texaco and Conoco-Phillips coal/water slurry feed gasifiers. The Shell dry gasifier uses a stream of powered coal injected tangentially and combusted with pure O_2 in an upward flowing water tube wall reactor which is coupled to a waste heat recovery boiler. Ash is collected at the base of the reactor and fly ash is separated downstream of the waste heat boiler (FIG. 2). The CO to H_2 ratio is high due to the limited quantity of water vapour present. The maximum current operating pressure is about 40 bar.

The GE/Texaco gasifier (FIG. 2) operates with a pumpable powdered coal in water slurry containing about 45% coal. This is quenched at the gasifier outlet with a liquid water stream, producing a syn-gas in which the temperature is reduced to the range 250°C to 300°C depending on the operating pressure. The Conoco-Phillips E-gas gasifier uses a two stage coal slurry injection followed by a waste heat boiler rather than a direct water quench. There is a large quantity of water vapour in the product gas from both of these gasifiers which gives a high H_2 to CO ratio. The presence of water in the reactor feed results in a lower dry gas efficiency for the GE/Texaco and Conoco-Phillips gasifiers compared to the Shell and UHDE gasifiers.



: Texaco Water Quench Type Coal Gasifier



: Shell Coal Gasification Process

FIG 2

		Dry entrained flow gasifier		Water quench gasifier	
		as produced	dry basis	as produced	dry basis
Gas composition					
H_2	mol %	30	32.3	15	39
CO	mol %	56	60.1	16	39.8
CO_2	mol %	1.5	1.6	7	18.75
Av	mol %	0.7	0.8	0.4	1
N_2	mol %	4.3	4.9	0.4	1
CH_4	mol %	0.2	0.2	0.1	0.2
H_2S	mol %	0.3	0.26	0.1	0.25
COS	ppm	200	215	Trace	Trace
HCN	ppm	100	110	Trace	Trace
H_2O	mol %	7	0.0	61	0.0
Pressure	barg	33		60	
Temperature	°C	250		240	

Table 1: Typical gas conditions following quench or heat recovery for both gasifier types

Both these gasifier systems require oxygen at 90% to 97% purity and at pressures depending on the gasifier technology. It should be noted that there is a trend towards higher gasifier operating pressures and 100bar systems may become standard in future. This will have a significant impact on the design of O_2 plants which are not required to deliver at such high pressures at present. High oxygen purity is not necessary since inert N_2 and Ar can remain with the H_2 fuel gas in an IGCC system with CO_2 capture, and be vented with the CO_2 free gas-turbine exhaust.

Table 1 shows the typical gas composition and condition for these two systems.

The Lurgi slagging gasifier is a fixed bed unit in which the reaction products of oxygen partial oxidation of the coal at the base of the gasifier flow upwards through the bed causing a de-volatilisation of the coal. Coals of all types can be used. The product gas contains condensable products such as coal tar, benzene, toluene, zylenes, and ammonia together with typically a 5% to 9% concentration of methane. There is a significant fraction of the carbon in the coal feed in the condensable and methane fractions which would need to be further processed in a separate gasification system to convert these fuels to H2 with the carbon converted to CO_2 for CO_2 capture. The residence time of coal in the gasifier is about 30 minutes which results in very large vessel sizes compared to the entrained flow gasifiers which have residence times of a few seconds. These features will limit application in the future.

2.2.3 Oxyfuel Systems

The combustion of a fossil fuel (or biomass) in oxygen results in high temperature product gas which contains CO_2 and H_2O plus any oxidised components present in the fuel such as sulphur which appears as SO_2/SO_3. Nitrogen and argon are mainly present due to impurities in the oxygen or air leaks into the system but some nitrogen may come from the fuel used. The combustion temperature can be moderated by recycling flue gas to the burner. Unlike air combustion, the concentration of excess oxygen and the combustion temperature can be independently varied. The CO_2 content of the dry flue gas can vary from about 70% to above 95% depending on the fuel, the process used, the air in-leakage, the O_2 purity used, and the excess O_2. The crude CO_2 is compressed to pipeline pressure and also purified to remove inert N_2, Ar, O_2, and acidic components such as SO_2, SO_3, NO/NO_2, HCI and HF (REF. 2).

The consumption of oxygen for a given heat output is much higher for an oxyfuel process than for pre-combustion CO_2 capture because the total oxygen required for combustion must be provided compared to a pre-combustion process where the hydrogen is burned in air in the gas turbine.

There are three types of oxyfuel systems which can be considered.

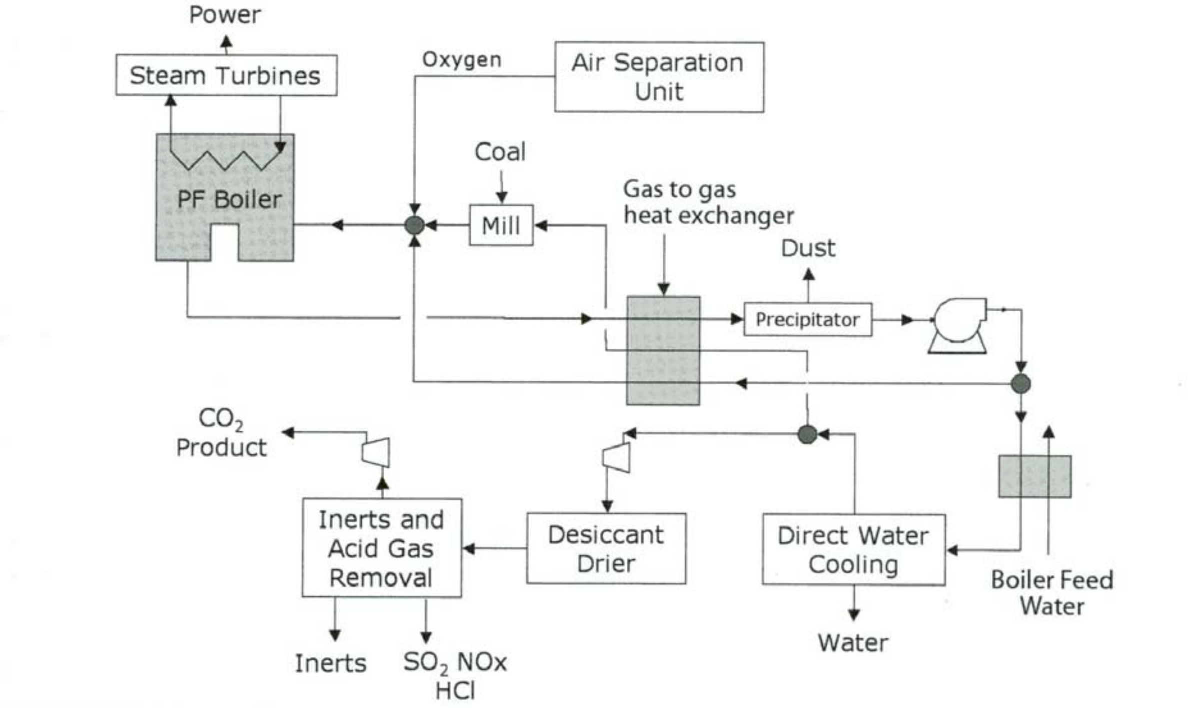


FIG 3

The first is the indirect heating cycle typified by a pulverised coal fired boiler which provides heat for a conventional steam cycle. The system shown in FIG. 3 includes the steps of oxyfuel coal combustion in a boiler with flue gas recycle, scrubbing of the nett flue gas product with water to remove soluble components such as SO_3 and SO_2, compression, desiccant drying and inerts and acid gas removal. The oxygen required for coal combustion can be provided at a purity of 90% to 97% at a pressure of about 1.7 bar abs. There will, in general, always be some air in leakage to the boiler, together with the need to use about 15% excess oxygen for complete combustion, which necessitates inert gas recovery from the CO_2. There is no benefit in using more expensive pure oxygen. A more complete process description is given in (REF. 2). The system of oxyfuel firing can be used both for new capacity and to retrofit existing boilers.

The second is the direct heating cycle (FIG. 4) which uses a gas turbine operating with recycle CO_2 in the compressor section followed by fuel combustion with the addition of pure oxygen and expansion of the $CO_2 + H_2O$ combustion products in the turbine section. The exhaust from the heat recovery steam generator is cooled to condense water vapour, and part is recycled, while the nett CO_2 product is purified and compressed to pipeline pressure.

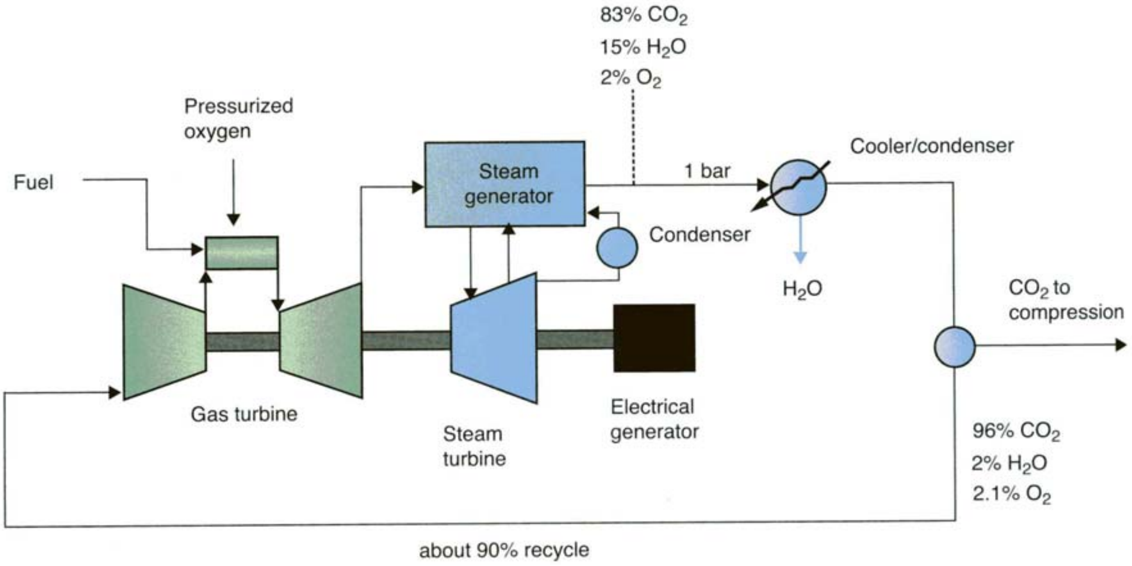


FIG 4

A complete description is given in (REF. 3). The system would only be suitable for natural gas fuel. The oxygen would be required at a pressure of about 40 bar and purity would be 90% to 97%. The system uses a higher pressure ratio in the gas turbine than a conventional air system while excess O_2 required for combustion means that an inerts removal step to purify the CO_2 is still needed. The CO_2 gas turbines required for this cycle have not yet been developed. A number of studies on advanced CO_2 gas turbine cycles with higher efficiency have been proposed (REF. 4). This type of oxyfuel cycle competes with the pre-combustion process which can use conventional air based gas turbines. There does not seem to be a significant cost or efficiency advantage for CO_2 gas turbine cycles.

The third is an oxyfuel cycle in which a fuel gas stream would be burned with pure oxygen and the combustion temperature would be moderated by injection of pre-heated liquid water (FIG. 5). Steam with about 10% to 15% CO_2 would be produced at any condition considered feasible for the turbine section. Conditions of say 1200°C and 400 bar might be possible. The high pressure steam is passed through a steam turbine with one or more oxyfuel reheat stages and the exit steam passes to a condenser where the CO_2 is recovered for drying and compression. Although this is a very advanced concept a 5 MW unit has been commissioned (REF. 31). The importance of this concept is its ability in theory to achieve efficiencies for electric power production with CO_2 capture using natural gas fuel of above 60% (L.H.V. basis). Oxygen must be produced at up to 400 bar pressure and 90% to 97% purity. Inert N_2 and Ar together with excess O_2 would be removed from the CO_2 during the compression process.

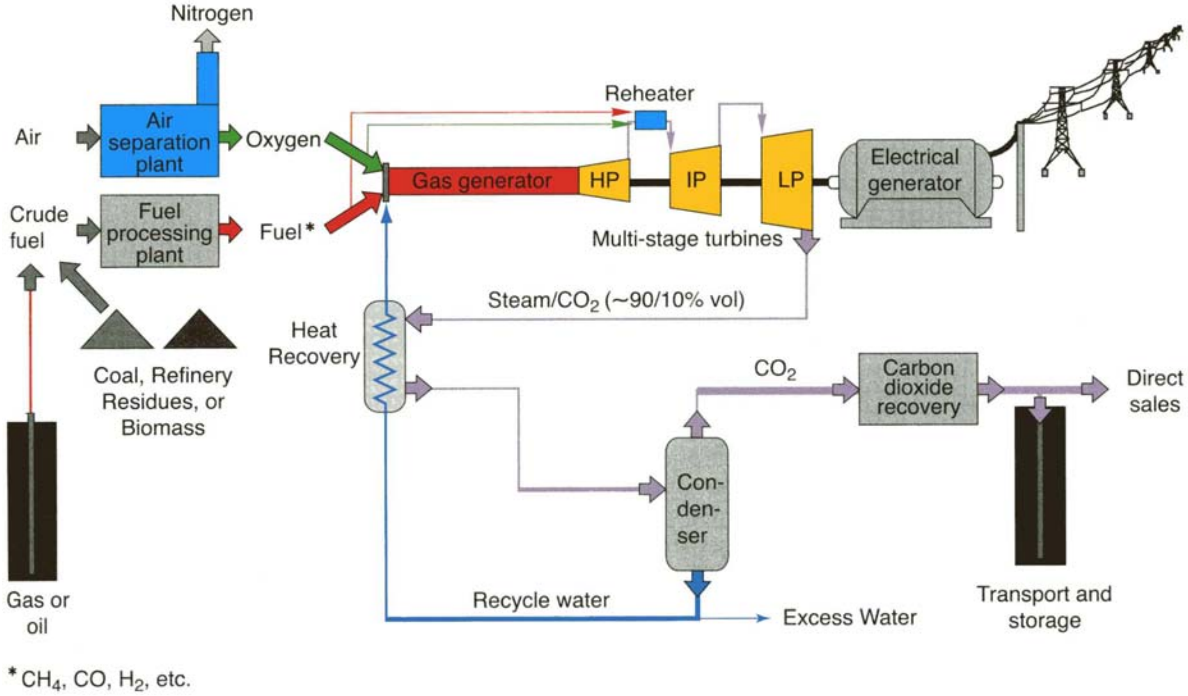


FIG 5

2.3 Nitrogen Requirements for H_2 Combustion in a Gas Turbine

Hydrogen has a low calorific value, a high adiabatic flame temperature when combusted in air, a wide flammability range, and a high burning velocity. In order to minimise NOX emissions when used as gas turbine fuel, it is normal to blend hydrogen with a diluent gas to lower flame temperature. When using cryogenic oxygen based pre-combustion decarbonisation processes for hydrogen generation, the diluent will generally be nitrogen gas, but some steam may also be present derived from low level heat recovery. It should be noted that there are many possible ways in which heat recovery in gasification/gas purification systems producing pure H_2 product can be made. The options for heat recovery are to produce steam for power production, or to heat H_2 and N_2 streams, or to humidify these streams. In each case the amount of steam used as H_2 diluent will be different but nitrogen dilution is generally the most efficient method. The gas turbine manufacturers have developed and demonstrated the capability of achieving efficient, stable reliable and controllable operation of their gas turbine combustion systems with ratios of H_2 to diluent in the range 0.4 to 0.6. With this fuel gas composition a NOX emission of 10 to 15 ppm in the gas turbine exhaust at 15% nominal O_2 concentration can be achieved. The nitrogen must be available at a pressure of typically about 5 to 6 bar above the gas turbine compressor discharge to overcome pressure drop in headers, burners and for the fuel gas control system. The maximum volume of nitrogen which could be used as a diluent in the H_2 fuel gas will in general be a little greater than the amount which could be separated from the air feed in the oxygen plant. This is generally the case even with a system in which the H_2 fuel gas and the nitrogen diluent streams have been humidified by direct contact with water heated using the maximum available low grade heat from the gasification/purification system. This means that the air separation plant will usually be designed for the maximum possible nitrogen recovery as pressurised gas for dilution of the hydrogen fuel gas.

The pressure of the nitrogen depends on the specification of the gas turbine manufacturer and is fixed by the control system requirements and the combustor design philosophy. If the nitrogen is mixed with the hydrogen feed up-stream of the gas turbine then it will be required at the same pressure as the hydrogen fuel gas. If the nitrogen is introduced separately into the head end of the combustion chambers, downstream of the hydrogen fuel control system, its pressure could be 2 to 3 bar less than the hydrogen fuel gas pressure. The method of hydrogen fuel gas combustion is characteristic of each manufacturer's gas turbines.

It is important that the oxygen content of the diluent nitrogen stream should be well below the lower flammable limit for H_2. A good objective is to design for 0.5% to 1% O_2 maximum in the diluent nitrogen stream. This low 0_2.content is generally available from a cryogenic oxygen plant which will be designed for an oxygen recovery of 95% to 98%. This low level of oxygen content in the nitrogen gives an adequate control margin for the ASU control system to respond safely to load changes during operation. When producing oxygen using a high temperature oxygen ion transport system the ITM module will be integrated with the gas turbine and H2 will be combusted in an O_2 depleted air stream with a reduced combustion temperature.

2.4 Systems with Power and Co-Products

The previous sections have concentrated on the oxygen based technologies used for electricity production with CO_2 capture. Syn-gas (H_2 + CO) derived from a gasification plant can be used for the production of a whole range of chemicals, hydrocarbon liquids and pure gases (REF5). For some of these systems, where unconverted syn-gas or H_2 is recycled, it may be desirable to specify high purity oxygen (99.5% to 99.8% purity rather than 90% to 95%) in order to reduce the amount of gas which must be purged from the system in order to limit the concentration of inert components such as argon in the circulating gas stream. Examples are the production of ammonia, which requires H_2, and methanol, and the Fischer Tropsch synthesis of hydrocarbon liquids which both require a 2:1 ratio of H_2 to CO. In each of these cases it will be necessary, in the case of cryogenic oxygen production, to balance the cost of extra purge gas processing against the extra cost of high purity oxygen production. The problem will not arise when using a high temperature oxygen ion transport system since this will produce high purity oxygen.

There is a strong possibility that high purity H_2 fuel will be required in very large quantities in the future for planned fuel cell powered vehicles and distributed power systems. This can be co-produced with electric power or as a sole product in any pre-combustion decarbonisation system using fossil derived fuel or biomass. The preferred method of H_2 purification is to use a multi bed pressure swing adsorption (PSA) system. Argon is a very difficult gas to remove in a PSA system. The O_2 purity will probably be 99.5% to 99.8% in this case.

2.5 Oxygen Requirements for Fossil Fuel CO_2 Capture Systems

Table 2 summarises the oxygen requirements for the oxygen consuming CO_2 capture technologies which have been briefly described.

TYPICAL OXYGEN REQUIREMENTS FOR POWER GENERATION WITH CO_2 Process	**Oxygen Flow Tonne/day/MWe**	**N_2 Fuel Dilution for Gas Turbine**	**Oxygen Pressure bar**	**Oxygen Purity Mol%**
Pf coal supercritical oxyfuel	19.5	No	1.5 to 2.0	95% to 97%
IGCC coal/water slurry gasifier	8.5	Yes max available	45 to 100	90% to 97%
IGCC dry entrained coal gasifier	7.1	Yes Max available	40 to 50	90% to 97%
Natural gas oxyfuel gas turbine combined cycle	15.5	No	30 to 40	95% to 97%
Natural gas combined cycle with H_2 fuel from auto thermal reformer	4.9	Yes Max available	30 to 40	90% to 97%

TABLE 2

The oxygen requirement per MWh of net electrical output for typical power stations burning coal or natural gas fuel with CO_2 capture is shown to illustrate the size of oxygen production facility required. The contrast between oxy-fuel and IGCC with pre-combustion decarbonisation is a factor of 2.5 and between coal and natural gas based pre-combustion decarbonisation is a factor of 1.6. The oxyfuel cases are recommended to be designed for a minimum of 95% purity to achieve the low power values without overloading the CO_2 with inert gas which must be separated. Any extra N_2 present in the oxygen used for pre-combustion decarbonisation will appear as a beneficial diluent in the H_2 gas turbine fuel stream.

3. OXYGEN PRODUCTION BY CRYOGENIC AIR SEPARATION

3.1 Introduction

The cryogenic distillation of air to produce pure oxygen together with nitrogen and argon is currently the only method available for the large oxygen production rates required for future fossil fuel gasification and oxyfuel combustion with carbon dioxide capture. The process was first developed by Carl von Linde in 1895 and improved by George Claude in the 1900’s to produce oxygen on a small scale for industrial processes such as welding, cutting and as a medical gas. Their efforts led to the founding of Linde and Air Liquide the two oldest and now the largest companies in the world producing oxygen and many other industrial gases and production systems. Many other companies exist today which are also active in the field of large scale oxygen production. The most important are Praxair, Air Products and Chemicals, and the Chinese companies such as Hangzhou Oxygen Company. The uses of oxygen and other air gases cover almost all industrial processes. The largest consumers are the steel, metallurgical, chemical, petrochemical, fertiliser and medical sectors. Recently new markets for very large quantities of oxygen have arisen based on the partial oxidation and reforming of natural gas to produce hydrogen and carbon monoxide gas ($2H_2 + CO$) for the synthesis of hydrocarbon liquids via the Fischer-Tropsch reaction. The current generation of plants under construction for this market are in the size range 3000 to 4000 tonne/day oxygen. Single train plants of up to 6000 tonne/day are being proposed for new facilities.

The production of oxygen by the cryogenic distillation of air has been under continuous development as an industrial process for over 100 years. The market is highly competitive and current technology ensures a system having the highest possible efficiency coupled to low capital cost and very high reliability. The future requirement for very large volume oxygen for oxyfuel and gasification systems used for electric power production and hydrogen transportation fuel will place new demands on the industry. A 2000 MW pulverised coal fired oxyfuel power station with all CO_2 delivered at high pressure to a pipeline would require about 40,000 tonne/day O_2 at 1.5 bar to 2 bar abs pressure and 95% purity (REF. 3). A coal gasification combined cycle power unit of 1700 MW output using GE/Texaco quench gasifiers and having four identical trains would require 14500 tonne/day O_2 at 65 bar abs 95% purity. These huge volumes of oxygen dwarf current installed capacity for industrial commercial and medical uses. In spite of the maturity of the technology, the industry will need to vastly increase production capacity and make efforts to further increase operating efficiency and reduce capital costs if CO_2 capture on a world scale is to be practiced in the future.

3.2 Physical Properties

The composition of dry air (neglecting rare gases and CO_2) together with the boiling points of the three major components nitrogen argon and oxygen is shown in table 3.

Component	**Composition Mol %**	**Boiling Point At 1 atm Pressure 0^oC**	**Boiling Point at 6 atm Pressure 0^oC**
Nitrogen (N)	78.12%	-195.8	-176.6
Argon (Ar)	0.93%	-185.8	-164.6
Oxygen (O_2)	20.95%	-182.9	-160.7

TABLE 3

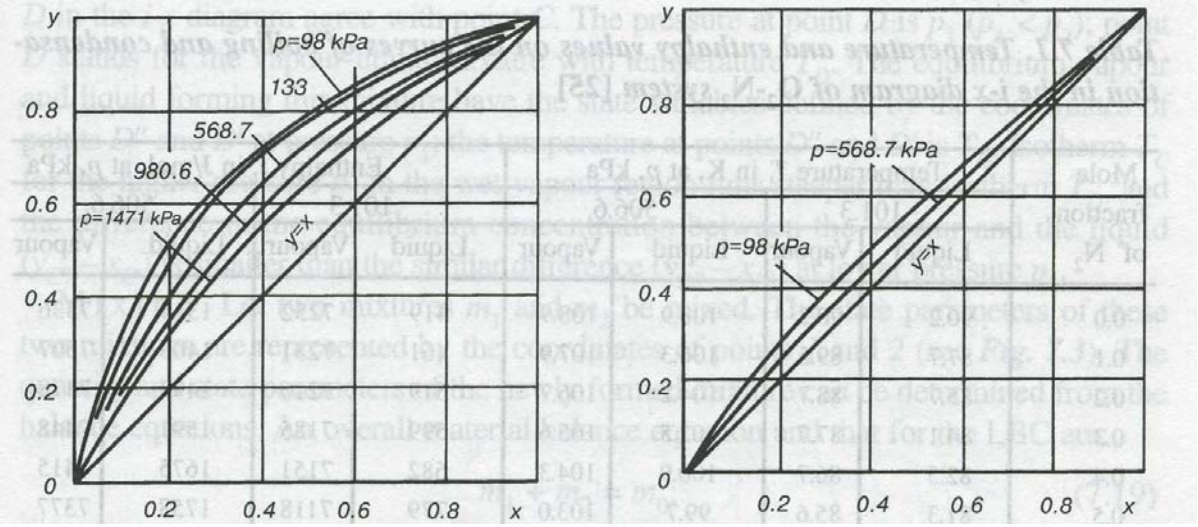
The CO_2 content is currently in the range 385 to 390 ppm.

The water vapour content varies with atmospheric temperature and elevation above sea level.

The hydrocarbon content, mainly methane is about 3 ppm, but local emissions may significantly increase this value.

The separation of air into oxygen and nitrogen depends on the relative volatility of the more volatile components N_2 and Ar relative to O_2.

The variation in vapour and liquid compositions for the O_2-N_2 and O_2-Ar systems as a function of pressure are shown in FIG. 6.



N_2/O_2 **Ar/O_2**

X is mol fraction N_2 or Ar in the liquid phase, y is mol fraction of N_2 or Ar in the gas phase

FIG 6

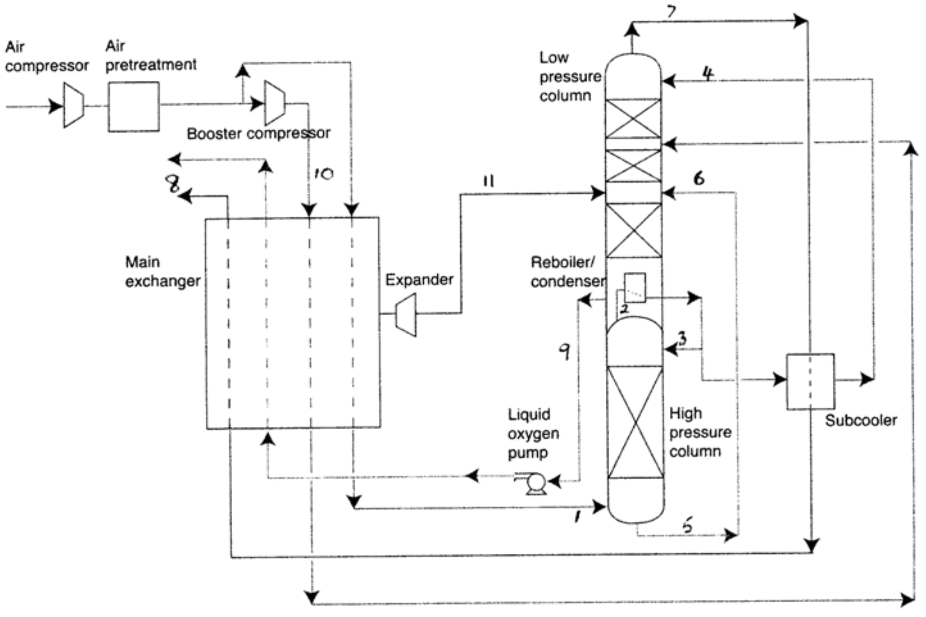


FIG 7

3.3 Oxygen by Cryogenic Distillation

The distillation of air to produce pure oxygen involves the separation of the more volatile components, N_2 and Ar from the less volatile component O_2. The oxygen will be collected at the base of the column, while the volatile components will leave the top of the column. In common with all distillation processes the separation is achieved by using a vapour feed to the base of the counter current separation section usually produced by a re-boiler and a reflux liquid flow to the top of the separation section, usually from an overhead condenser. FIG. 7 shows a basic cryogenic air separation plant (ASU) which still uses the column arrangement devised by Carl von Linde in 1895. The system is characterised by a double distillation column with the two columns separated by a re-boiler condenser. The function of the lower column is to provide the re-boil and reflux for the upper column in which the separation of air into its components takes place.

Air at a pressure of typically 4 to 6 bar and at its dew point, or sometimes partially liquefied, enters the base of the lower column at 1. The vapour rising counter currently to down-flowing liquid is enriched in nitrogen and enters the re-boiler condenser as pure nitrogen, 2, where it condenses. The liquid nitrogen produced is divided into two streams. Part 3 returns to the top of the lower column as reflux, the remainder 4 is used as a reflux stream at the top of the upper column. The liquid stream leaving the base of the lower column 5 containing 35% to 40% oxygen is fed into the middle section of the upper column at 6. The upper column separates the air feed into a pure O_2 fraction, taken from the base of the column and a gaseous nitrogen fraction 7 leaving the top of the column. The nitrogen stream passes through a heat exchanger which sub-cools the two liquid streams 4 and 6 together with the crude liquid oxygen stream 5 to minimise the fraction of liquid which vaporises when the pressure of these streams is reduced as they enter the upper column.

The gaseous nitrogen stream together with the product oxygen stream is heated to near atmospheric temperature in the main heat exchanger against incoming air and exits the plant at atmospheric pressure. The pressure above atmospheric at the base of the upper or low pressure (LP) column is simply the pressure imposed by the pressure drop through the distillation column plus the pressure drop in the gaseous nitrogen circuit. This pressure defines the boiling temperature of the oxygen in the re-boiler. The amount of surface area and the heat flux in the re-boiler defines the temperature difference between the boiling O_2 and the condensing N_2 and hence defines the condensing pressure of the N_2. The pressure drop through the lower or high pressure column, plus the pressure drop through the total air feed circuit defines the discharge pressure of the feed air compressor.

The oxygen production can be withdrawn from the base of the LP column either as a liquid or a gas. Most modern plants now withdraw all O_2 production as a liquid which is pumped to its required pressure in a multi-stage centrifugal liquid oxygen pump 9. In order to maintain a heat balance on the main heat exchanger and the distillation column systems, it is necessary to vaporise this liquid oxygen stream in the main heat exchanger against a condensing liquid air stream. This results in the necessity of taking about 30% of the feed air and compressing it further in a booster air compressor 10 to a pressure which gives a positive temperature difference for condensation of this air in the main heat exchanger. For oxygen delivery at 65 bar, this pressure would be in the range 60 bar to 90 bar.

The heat exchangers, distillation columns, pumps and all other piping and equipment operating below atmospheric temperature are contained in a metal jacketed insulated container called a cold box. The refrigeration required to maintain a heat balance for the cold system is made up of heat leak into the cold box and the enthalpy difference between all streams entering and leaving the cold box. This net refrigeration load is balanced by a heat rejection from the cold box in the form of shaft power produced by a high speed turbine which expands a small air stream 11 from high pressure into the LP column.

The waste nitrogen leaving the cold box has practically zero water vapour content. This gas stream can be passed through a direct contact tower counter-currently to a cooling water stream producing a chilled water stream by a process of evaporative cooling. The main air compressor discharge flow is cooled in a two section direct contact tower packed with plastic packing firstly against cooling water then against chilled water. The air temperature is typically reduced to $9^{o}C$ to $12^{o}C$ by this operation which reduces the water vapour content.

The air is then purified to remove components such as water vapour and CO_2 which would freeze and block the cryogenic sections of the plant and trace components such as unsaturated hydrocarbons and nitrogen oxides which could have undesirable safety related effects on plant operation. The air purifiers consist of a pair of adsorber vessel containing layers of adsorbent which are switched over in sequence and regenerated periodically using heated nitrogen gas.

It should be noted that it is possible in any cryogenic air separation plant, irrespective of the main products to produce by-product streams of oxygen, nitrogen and argon at any purity in gaseous or liquid form. In particular it is a simple process to increase the refrigeration produced by the expansion turbine to allow a small quantity of liquid O_2 or N_2 to be accumulated in storage tanks and used either as a back-up system for plant outages or to give rapid start-up for the air separation plant.

3.4 The Design Factors Affecting Oxygen Cost

The pressure balance and the re-boiler condenser design are the key features which control the air compressor discharge pressure and therefore fix the power consumption for the cryogenic oxygen plant. In the basic Linde double column configuration, the power consumption can be minimised by increasing the size of the heat exchangers to reduce pressure drop, by increasing the size of the re-boiler condenser to reduce temperature difference between boiling oxygen and condensing nitrogen and by using structured packing in the two distillation columns to reduce pressure drop. Typical air compressor discharge pressures would be in the range 4.5 bar to 6 bar.

The power will also depend on the oxygen purity chosen. For oxyfuel and IGCC applications, where 90% to 97% oxygen purity is required the boiling O_2 temperature in the re-boiler condenser is lowered by the presence of N_2 and Ar compared to pure O_2 which is typically in the range 99.5% to 99.7% O_2 for industrial applications. This gives a lower air compressor discharge pressure.

Referring to Section 1.2 it can be seen that argon has an intermediate boiling point between nitrogen and oxygen and that the relative volatility of argon is much lower than nitrogen. This leads to a major difference in the separation of pure oxygen (>97%) and impure oxygen (<97%). For purities of >97% O_2, the lower section of the low pressure column firstly strips out all the nitrogen then separates Ar from O_2. For say 99.6% O_2 purity this results in a very large increase in the number of separation stages required in the upper column. In a simple double-column system this would typically be about 35 stages for 95% purity increasing to about 60 stages for 99.6% purity with between 95% and 98% of the oxygen in the air feed being produced as oxygen product in each case. The choice of 90% to 97% O_2 purity for large O_2 plants required for CO_2 capture systems results in lower capital cost and lower operating cost compared to high purity oxygen. The oxygen recovery from the air feed can be increased by increasing the number of separation stages in the distillation columns but this must be balanced against the increase in the air compressor discharge pressure. Careful optimisation is required for each specific design case.

The design of the cryogenic oxygen plant depends on the value of power used. A major factor for CO_2 capture systems is the large increase in the cost of power generation. A study (REF 3) of a 600 MW pulverised coal oxyfuel power plant showed an electricity cost increase from 4.9 to 7.28 US cents/kWh. In this case, the oxygen plant had a capacity of 10,373 tonne/day at 95% purity with a power consumption of 87 MW (201.3 kWh's/tonne O_2). The capital cost of the ASU was 258 million $ US. Taking a 10% capital charge/year and 7500 hrs/year operation, the power cost was 47.5 million $ US/year and the capital charge was 25.8 million $ US/year. In this case the cost of power is 65% of the cost of oxygen.

The power cost for cryogenic oxygen production is a very high proportion of the current cost of oxygen. This has led to a huge effort by industrial gas companies to devise improvements to the basic Linde double column cycle. There are a large number of patents showing a variety of designs which have lower specific power consumption. Subsequent sections will present some of these which are relevant to CO_2 capture applications, where even higher efficiency plants with higher specific capital costs will be justified. A second area where costs have been reduced is by integration of the cryogenic air separation plant air and product gas compression systems with the basic power production process. The third area of development is in the design of the basic components of the cryogenic oxygen plants; the compressors, the air purifiers, the heat exchangers and the distillation columns.

3.5 Components of a Cryogenic Oxygen Plant

3.5.1 The Gas Compression System

The large cryogenic air separation systems required for CO_2 capture processes will usually be based on a pumped oxygen cycle. This requires a main air compressor of 3.5 bar to 5.5 bar discharge pressure depending on the cycle design and plant economics. The air booster compressor will further compress about 30% of the air to a pressure of 6 bar, when oxygen is required at 1.7 bar for an oxyfuel coal fired boiler, or to a pressure in the range 60 to 90 bar when producing oxygen at 40 bar to 70 bar for a fossil fuel gasification process. Multistage centrifugal oxygen compressors used in the past with low pressure oxygen gas inlet flows have now been largely superseded by the pumped liquid oxygen cycles. These cycles avoid potential oxygen compressor fires and have a 1% to 2% better specific power consumption plus a reduction in capital cost due to reduction in heat exchanger size and substitution of a much cheaper air compressor for an expensive oxygen compressor.

The very large air flows required for O_2 plants in the range 2,500 tonne/day to 6,000 tonne/day necessitate the use of an axial flow first stage followed by multiple centrifugal stages. The compressors can be driven by electric motors or steam turbines. For IGCC applications, a nitrogen booster compressor may be required to provide diluent gas for the H_2 gas turbine fuel. This compressor will be a multistage integrally geared machine of standard design. The compressor manufacturers have ample knowledge and experience to produce machines of very large throughput. At present, demonstrated capability extends to a 4,000 tonne/day O_2 plant size. Single train machines for 10,000 tonne/day O_2 capacity can be built now with low risk given market demand for CO_2 capture power systems.

3.5.2 The Air Purification System

The air entering a cryogenic plant must be purified to remove mainly CO_2 and H_2O which would deposit as solids in the heat exchangers. Other critical impurities are hydrocarbons, particularly trace quantities of acetylene and other un-saturates and nitrous oxide which can accumulate with trace CO_2 in the oxygen side of the re-boiler. The CO_2 and H_2O are removed by adsorption on solid adsorbent pellets contained in a dual vessel system which is switched at regular intervals at typically 90 min to 6 hrs cycle time between an on-line period and a thermal regeneration and cool-down period. The beds are regenerated by a counter-current flow of heated waste N_2 gas followed by a cool-down period. The adsorbents used are alumina, zeolites with high CO_2 adsorption capacity and also proprietary modified adsorbents with activators to improve performance such as alumina with added alkali metal or ammonium compounds including hydroxides, carbonates, bicarbonates, phosphates and organic acid salts (REF. 6). These modified aluminas are particularly useful as they have an excellent capacity for CO_2 as well as water vapour and they can be regenerated at temperatures below 150°C. They are used as a first layer in the bed with a second smaller layer of 13X zeolite which removes traces of CO_2 and hydrocarbons. The preferred bed geometry for very large air flow rates is an annular bed arranged vertically within the pressure vessel. The air flows radially inwards towards the central collection tube while regeneration gas flows radially outwards from the centre mandrel. This arrangement results in a compact layout of equipment.

3.5.3 The Cryogenic Heat Exchangers

Cryogenic air separation plants use aluminium plate-fin heat exchangers for all cryogenic heat transfer duties except high pressure oxygen vaporisation, where stainless steel is an option for strength and safety considerations. The geometry of the heat exchanger blocks is shown in FIG. 8 which gives the structural layout of a single passage and FIG. 9 which gives the layout of a complete block having three streams A, B, C. The passages are up to 1.4 metre wide with fin heights of 5 mm to 9.5 mm and up to 7 fins per centimetre width, and a total block height of up to1.4 metre. The maximum block length is about 8 metres. The surface area available in the heat transfer section is up to about 1500 m^2/m^3 block volume. In FIG. 8 the stream A enters and leaves via gas distribution Section 3 which evenly distributes the gas flow across the heat transfer passage 2. The passage is bounded by sealing strips 4. The passages are stacked as shown in FIG. 9 with end tanks 6 collecting flows from each stream and fitted with inlet and exit nozzles 7. Up to 6 streams can easily be accommodated for simultaneous heat transfer in each block. The aluminium blocks are assembled from the many component parts in a jig which is placed in a vacuum brazing furnace. The component parts are coated with a silicon/aluminium brazing alloy layer which is a eutectic with a melting point below that of aluminium.

The blocks for the main heat exchanger are arranged vertically in a battery with individual stream nozzles connected to large manifold pipes which distribute or collect the fluid streams entering or leaving the blocks.

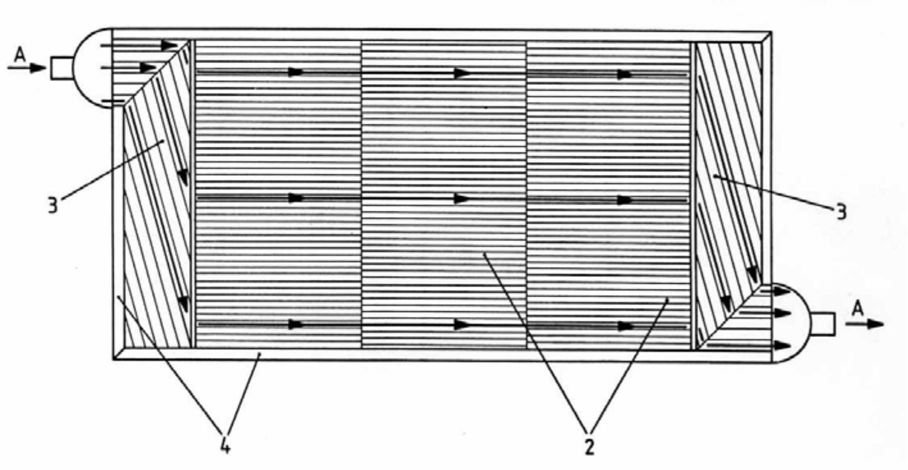


FIG 8

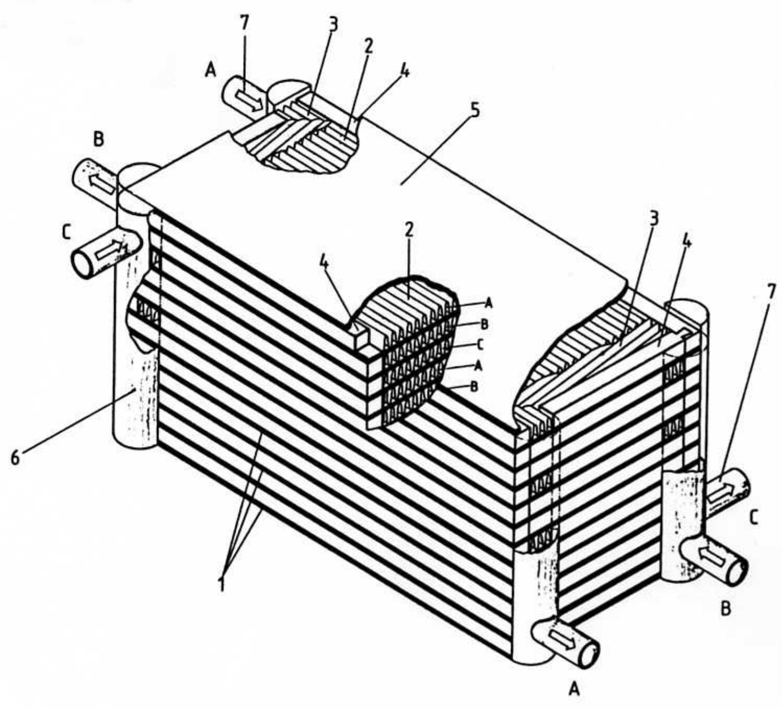


FIG 9

A 6000 tonne/day O_2 plant might need 50 to 60 blocks for an economic design with high power value. Aluminium plate fin blocks are also used for the sub-coolers and re-boiler condensers.

The key feature of these plate fin heat exchangers is the huge specific surface area available, the ability to provide very low temperature differences in the heat exchangers for high efficiency and the low cost per unit of heat transfer area provided. Temperature differences of 1^oC can be achieved in the re-boiler condenser and 2 to 3^oC at the warm end of the main heat exchanger.

Plate fin heat exchangers can also be constructed in stainless steel using either vacuum brazing or diffusion bonding at high temperature. A high pressure liquid oxygen vaporising heat exchanger in stainless steel has a much higher resistance to combustion than aluminium. The reaction between high pressure oxygen and aluminium is explosive in its intensity given a source of ignition. The design of an intrinsically safe stainless steel heat exchange for high pressure oxygen is shown in (REF. 7).

The world production capacity for aluminium plate-fin heat exchangers will need to be significantly increased to meet any future demand for power and H_2 supply systems with CO_2 capture using oxyfuel or gasification technology. The current block maximum cross-section is limited by the conduction of heat to the centre of the block to achieve adequate brazing quality and strength without causing the aluminium alloy to suffer changes in its crystal structure. Larger block cross-section with significantly fewer blocks headered into the main heat exchanger battery would lead to a useful cost reduction.

The Russian firm of Cryogenmash has proposed and tested a brazing procedure which uses a circulating stream of heated argon gas in a furnace operating at atmospheric pressure to heat the core by convective heat transfer within the passages. Cores of very large cross section could be manufactured in this way with significant saving in headering manifolding and pressure drop.

3.5.4 The Distillation Column

Most modern cryogenic air separation plants use structured packing for the mass transfer sections of the distillation columns. Packing has the characteristic of lower pressure drop per theoretical separation stage compared to distillation trays which were used exclusively up to about 1990. The saving in air compressor power consumption makes packing the natural choice for all cryogenic O_2 plants used with future CO_2 capture systems since CO_2 capture inevitably increases power costs above their already high levels by 20% to 60%.

Packing is generally fabricated from thin aluminium sheet material which is perforated, stamped with a mini-corrugated surface texture then folded into V shaped geometry, cut into strips which are stacked and secured with wire bands to form large packing sections. These sections are profiled to fit snugly together within the circular column (FIG. 10). The V shaped folding of the packing runs at an angle of 30^oC to 60^oC from the vertical. The direction of the slope alternates left then right on each sheet of packing in a stack. The spacing and angle of the V indentation, the height of each layer and the micro surface structure are modified to give a surface area from $250m^2/m^3$ to over 1000m2/m3 of packing volume. Each large pack of sheets is assembled in the column in a layer about 200mm thick.

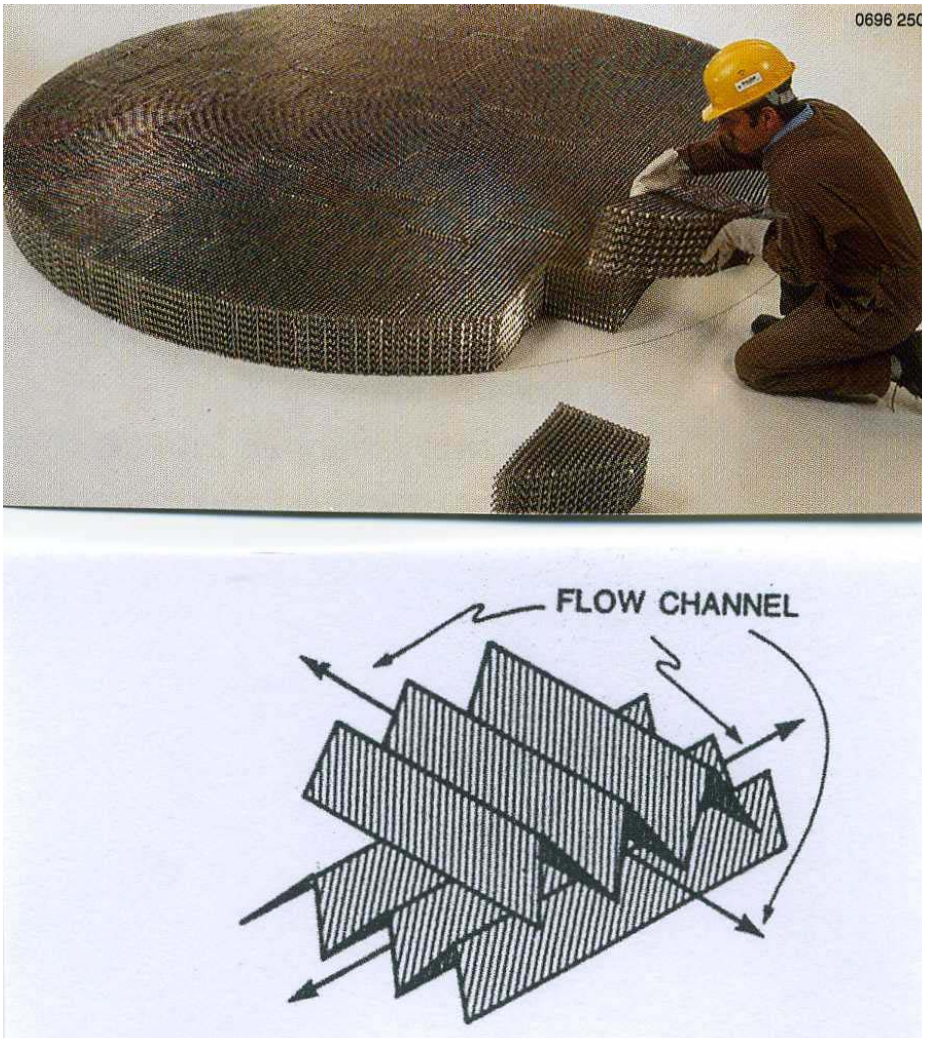


FIG 10

Each layer of packing is rotated relative to the layer below by up to 90 degrees to assist vapour/liquid mixing and to secure even flows in the column. The sections which bear against the internal wall of the column are fitted with edge sealing strips to prevent liquid by-passing the packing.

Structured packing can be purchased commercially from companies such as Sulzer and Koch, but each of the major industrial gas companies, Air Products and Chemicals, Linde and L’Air Liquide manufacture their own packing with their own geometry developed and optimised specifically for cryogenic air distillation conditions.

Of particular importance is the design of liquid distributors which must ensure accurate and even distribution of liquid across the packing cross-section. Considerable development efforts have been made to optimise the total packed column distillation system which is now able to give excellent performance for virtually any column throughput and size. Current industry experience includes shop built packed columns with up to 200 stages for argon purification and column diameters of 6 metre.

There is really no limit on column diameter. A 10 metre column could be built equivalent to a 10,000 tonne/day O_2 plant with low process and mechanical risk. The major consideration would be the difficulty of shipping and the necessity to install all packing and column internals on site.

3.5.5 The Re-boiler Condenser Unit

Re-boiler condensers are generally installed within the shell of the distillation column. Aluminium plate fin heat exchangers were first used for this duty in the early 1960's. The method of utilisation was to submerge the 2 metre to 3 metre long heat exchange blocks in a pool of liquid oxygen in the base of the low pressure column. The oxygen passages were open ended. The nitrogen passages were headered together so that nitrogen gas could pass from the top of the high pressure column to the top of each block and condense with downward flow and withdrawal of liquid nitrogen from the base of each block. This arrangement gives a temperature difference of about 2.2°C across the re-boiler. An improved arrangement is to collect liquid below the bottom LP column packing section and introduce this liquid evenly into the top of each of the heat exchange blocks so that the liquid oxygen flows in a downward direction as it boils. This gives a lower boiling pressure and boiling temperature for the oxygen compared to the submerged re-boiler arrangement which is subject to a hydrostatic head of liquid oxygen. The core length for the down flow re-boiler can be in the range of 5 metre to 8 metre allowing more surface area within a given column shell diameter. The temperature difference can be as low as 1°C.

Safety is a critical factor in re-boiler condenser design and operation. It is critical that every part of every passage on the oxygen side of the re-boiler has an adequate flow of liquid. Dry boiling must not occur. Certain hydrocarbons such as acetylene can deposit as solids which can be very easily detonated even at cryogenic conditions. The presence of CO_2 and N_2O in the liquid oxygen must be well below the solubility limits. There must be adequate flow of liquid oxygen in each passage to prevent the accumulation of solid deposits which would cause blockage and dry boiling of the liquid oxygen. The accumulation of hydrocarbon residues has in extreme cases caused sufficient energy release to cause a secondary catastrophic explosive reaction between the oxygen and the aluminium block material which can destroy the cold box. This eventuality is preventable by careful design of the liquid oxygen distributors and by specifying and designing the front end air purifiers for extremely low exit concentration of CO_2, N_2O and critical hydrocarbons, and by having adequate purge of liquid oxygen from the column sump. A pumped liquid oxygen compression system is a significant advantage in ensuring safe plant operation.

A penalty in using down flow re-boilers is the much longer column sump which is required due to the increased block length, and the necessity of providing a disengagement space for vapour and liquid and a liquid sump at the base of the low pressure column. This may mean that the low pressure column and high pressure column may need to be built side by side rather than with the LP column and re-boiler mounted in one shell vertically above the HP column.

The large O_2 plants needed for CO_2 capture systems will have down flow re-boilers, probably with maximum available 8 metre block lengths to achieve the lowest possible temperature difference. There is no significant process, safety or mechanical risk in increasing single train plant capacity.

3.6 Integration of the Cryogenic Oxygen Plant and the Electrical Power Generation System

3.6.1 The Oxyfuel Process

A conventional pulverised coal fired boiler, using a Carnot cycle steam system requires an array of condensate and boiler feed water heat exchangers to pre-heat the boiler feed water to a temperature near to its boiling point, or to a temperature near 300°C in the case of a super critical boiler, before the boiler feed water enters the boiler. This heating is accomplished by condensing steam, which is bled from the steam turbines at progressively increasing pressures to minimise the power penalty on the system. There is efficiency and capital cost benefits available by adiabatically compressing the ASU feed air and using the heat of compression for condensate and first stage boiler feed water pre-heating. This allows more steam flow in the steam turbines and the increase in electrical output is greater than the difference between the power consumption of isothermal compared to adiabatic air compression. Other benefits are the much lower capital cost of the adiabatic air compressors and the elimination of most of the cooling water duty required for a conventional isothermal air compression system. The absence of compressor intercoolers means that the air compressor casing does not need intermediate air inlet and outlet connections. The compressor can be built on a much smaller and simpler foundation with no need to elevate the compressor to make room for the intercoolers underneath the compressor casing.

3.6.2 Gasification Systems – Integration with the Gas Turbines

The air compressor of a gas turbine can be used as a source of part or all of the air feed to a cryogenic air separation plant. This application is a key feature of any fossil fuel gasification process which will be producing H_2 or H_2 + CO fuel for a gas turbine combined cycle system. The ASU has the requirement not only to produce O_2 for the gasifier but also to supply all the available waste nitrogen from the ASU for diluting the H_2 or H_2 + CO fuel to the gas turbine. The nitrogen is required at the fuel gas pressure of over 20 bar for a large industrial gas turbine. The N_2 compressor power is a significant parasitic power on the system. There are three major options for air integration between the gas turbine and the ASU:-

3.6.2.1 Total Air Integration

All the ASU feed air is supplied from the gas turbine air compressor discharge. This system was used on the Demkolec coal based system at Buggenum, Netherlands. The control of the ASU with fully integrated air compression is quite difficult. The problem arises when the gas turbine load is varied. An increase in power output results in an increase in the air pressure from the gas turbine. This pressure increase is then transmitted to the ASU which causes the boiling points of all liquids to rise, so liquids in the column system would become sub-cooled and net vapour flows would reduce just at the time when extra O_2 flow was require for the combustion of extra gas turbine fuel. The converse can occur if the gas turbine load is reduced. Air pressure falls and excess flows of gas are generated in the column system by flash vaporisation of the boiling liquids just when, in this case, less O_2 is required. The nitrogen purity must not be allowed to vary from strict tolerance limits of less than about 2% O_2 content, as this N_2 will be used as a diluent for the gas turbine fuel and higher O_2 concentration risks a dangerous energy release. The only satisfactory method of operation with any ASU air flow derived from the gas turbine air compressor is to reduce the air pressure available to a pressure required by the cryogenic ASU and to carefully control this pressure. This ASU demand pressure will vary over a predictable range defined by the variation in O_2 demand between maximum and minimum ASU design points. The most efficient means of pressure reduction is to use a power producing expansion turbine. A further problem with total air integration is the necessity to run the gas turbine on natural gas or liquid hydrocarbon fuel to provide air for the ASU during start-up of the ASU and the gasification system.

Current large industrial gas turbines have an air compressor discharge at about 18 bar and a temperature of about 435^{O}C. There must be an efficient heat exchange between the air exiting the pressure reduction expansion turbine and the ASU product N_2 and O_2 streams to conserve this heat within the process streams which make up the gas turbine expander flow. The Demkolec plant control system was shown to operate satisfactorily during power ramping in spite of the problems caused by the variation of feed air pressure to the ASU.

Future gas turbine systems, such as the GE H frame machines, use steam cooling for the high temperature turbine blades and other components rather than air bled from the compressor section. The H frame has a firing temperature in the range 1400^{o}C to 1450^{o}C which has resulted in an optimised pressure ratio for the air compressor of about 22. Air can be withdrawn from the gas turbine compressor discharge via ports in the combustor cans. The quantity of air extracted for the air separation plant depends on air feed conditions of temperature, pressure and humidity and the volumetric flow of diluted fuel gas used. The objective in optimising the design is to load the turbine section with the maximum flow of gas consistent with the design limitations of the gas turbine.

3.6.2.2 Partial Air Integration

Part of the ASU feed air flow can be provided by the gas turbine as bleed air from the compressor discharge. The amount taken depends firstly on the minimum air flow required for plant start-up, which would be supplied from a separate air compressor, and secondly the amount of air available from the gas turbine, which depends on its design and on the atmospheric conditions. Typically 50% of the feed air could be supplied from the gas turbine air compressor section, preferably with a pressure let down using a power producing expansion turbine and appropriate heat recovery from the gas turbine air feed. A separate electric motor driven inter-cooled air compressor would supply a minimum 50% to 60% of the air flow required by the ASU. This arrangement allows the start-up of the ASU and the gasifier to take place before the gas turbine system is started. This process is used on the Elcogas IGCC system at Puertolano in Spain.

The overall magnitude of air side-draw flow available from the gas turbine will depend on a number of factors. The ideal situation is to ensure that for the gas turbine model being considered, the overall loading of the expander section is maximised. Since the diluted H_2 fuel gas (for a CO_2 capture case) will have about 50% H_2, the fuel gas flow will be 7 to 8 times greater than the case with natural gas fuel. This extra flow may mean that it is necessary to vent air from the compressor section in order to limit flow to the expander section. This is the air flow available for air side-draw to be used for ASU air feed. The system must be optimised for each location since atmospheric temperature pressure and humidity have a significant effect on the air compressor flow rate.

3.6.2.3 No Air Integration

The case for zero air flow from the gas turbine is only optimum for situations in which there is limited air flow available from the air compressor due to hot elevated locations, or where there is a significant design margin available in the gas turbine allowing extra fuel gas flow. In the latest large gas turbine models available from manufacturers the margin for extra fuel gas flow at ISO conditions is limited, and cases in which only nitrogen fuel gas dilution is used will depend solely on atmospheric conditions.

3.7 Process Cycles Used for Cryogenic O_2 Plants for Carbon Dioxide Capture

There are a number of different duties for cryogenic O_2 plants designed for CO_2 capture procedures. These duties are summarised in Table 2 of Section 2, which describes the CO_2 capture technologies which are major users of oxygen. The main features of these oxygen requirements are the very large O_2 production rates required and the high power cost when CO_2 capture is used. This high power cost dictates the selection of process cycle used in the cryogenic O_2 plant. We should choose the most efficient process possible having due consideration for capital cost.

3.7.1 Factors which Affect Power Consumption

A thermodynamic analysis of energy of the streams passing through a cryogenic air separation plant reveals the contribution of each part of the process to the overall power consumption.

Exergy is defined as the work obtainable from a mass of a substance by virtue of its pressure, temperature, or composition being different from a defined reference state, which could be ambient conditions. Its usefulness is in computing the minimum amount of work required to go from an initial to a final state (for physical change)

$$\text{Exergy } B = \quad H - To\ S \qquad (3.1)$$

Where H is the enthalpy,T_o is the reference temperature, S is the entropy.

Any shaft work W into the process must be included plus any heat input Q_H evaluated as the Carnot heat equivalent

$$Q_C = Q_H (1 - T_O/T_H) \qquad (3.2)$$

For heat Q_H supplied at temperature T_H.

For a given part of the overall process the actual work of that part which contributes to the overall work of the process is.

$$\Delta w_o = (\Delta H - T_O \Delta S) + (Q_H (1 - T_O/T_H) + W) \qquad (3.3)$$

For the overall process, the actual work required

$$W_o = \Sigma\ \Delta B + W_{\acute{L}} \qquad (3.4)$$

Where $W_{\acute{L}}$ is the extra separation work of the process, sometimes referred to as lost work.

These calculations are generally available as a sub-routine in standard flow sheeting calculation programs such as ASPEN PLUS. Exergy analysis has been used extensively in the cryogenics industry to analyse process systems and improve performance.

The breakdown of contributions to total plant power consumption for a simple 99.5% O_2 purity oxygen production plant with gaseous delivery at near atmospheric pressure and having a simple Linde double column is shown in TABLE 4. The major contributors to the inefficiency of the process are the air compressor, the low pressure distillation column and the heat exchangers (both temperature difference and pressure drop). The latest axial flow compressors have an adiabatic efficiency of about 90%. In the case of the oxyfuel coal fired boiler where the heat of compression is used for boiler feed-water pre-heating this combination gives a significant overall reduction in lost work.

TABLE 4

ITEM	**% CONTRIBUTION TO TOTAL POWER**
Main heat exchanger	9.6
Re-boiler condenser (2.2°C temperature difference)	4.3
Expansion Turbine	0.9
Sub-coolers	1.9
HP column(trays)	3.2
LP column(trays)	16.8
Heat leak	0.9
Piping pressure drop	5.7
Pressure reducing valves	3.4
Mixing	0.4
Air compressor (isothermal efficiency = 71%)	
Motor	27.6
Ideal work of separation	3.3
Product conditions	16.9
WORK INPUT	5.1
	100%

The use of down-flow re-boilers gives a temperature difference in the re-boiler condenser to less than 1°C, more than halving the lost work. Optimising the amount of surface area in the main heat exchanger will reduce lost work while optimising overall cost. The use of packing in the distillation columns will minimise pressure drop.

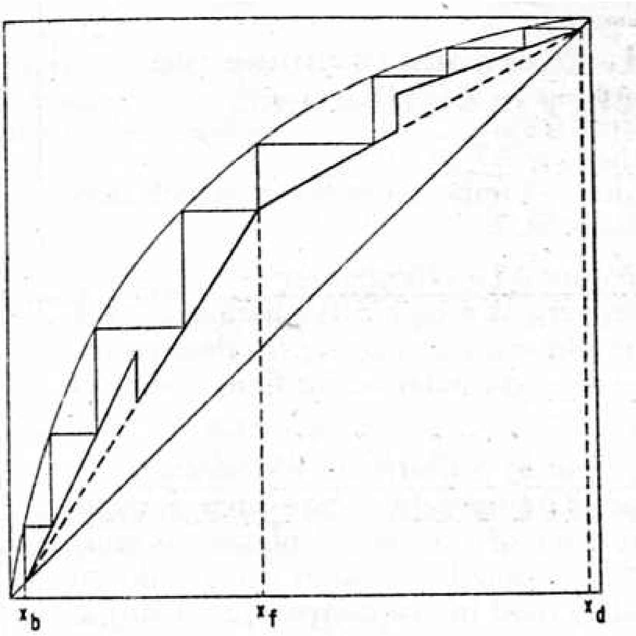
The major changes which can be made in the process cycle to reduce losses and increase efficiency are the result of considering how the low pressure column distillation process can be improved. This will also impact other areas of loss.

3.7.2 More Efficient Air Distillation

The process of air distillation to produce O_2 at purities up to 97% O_2 is essentially a binary distillation to separate nitrogen and oxygen. FIG.6 shows the McCabe-Thiel diagram for the LP column of an ASU based on the N_2/O_2 separation with the equilibrium lines from 0.98bar to 14.71 bar shown. The major factor affecting the efficiency and lost work for distillation is the mixing of fluids having different compositions in a theoretical separation stage. This difference is measured by the relative change in composition across the separation stage, which is measured by the vertical and horizontal separation between the operating and equilibrium lines on the McCabe-Thiel diagram. Two major methods can be used to increase the efficiency of the separation:-

- The pressure of the LP column is raised by back-pressurising the plant. This has the effect of moving the system to lower relative volatility of nitrogen to oxygen and, as can be seen in FIG. 3, it flattens the y-x curve and moves it closer to the 45^{o} line. This reduces the mixing inefficiency in each stage of separation. The practical embodiment of this principle is the pressured column cycle. This has an identical flow sheet to FIG. 7. The only difference is that the back pressuring of the plant results in the production of all the nitrogen and oxygen separated from the air at elevated pressure while the air inlet pressure must be significantly increased. This cycle can be used for IGCC plants where all the separated oxygen is used for gasification of a fossil fuel and all the nitrogen is used as a diluent for the H_2 or (H_2 + CO). This was the cycle used for the Demkolec IGCC plant.

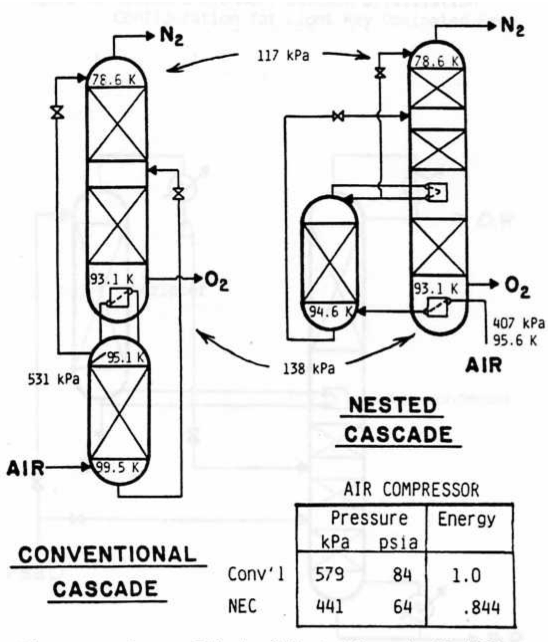
- The use of additional re-boilers or vapour feed points in the bottom section of the column or additional condensers or liquid reflux points in the top section of the distillation column causes the operating line to move closer to the equilibrium line, thus reducing mixing losses and increasing efficiency. This is shown in FIG. 11 where the effect of an intermediate re-boiler and an intermediate condenser on the position of the operating lines in the column are shown (REF. 8). It can be seen that the operating and equilibrium lines move closer together which reduces the mixing losses in the distillation system but at the expense of an increase in the number of theoretical stages and an increase in capital costs



X axis is mol fraction of the more volatile component in the liquid and the y axis in the vapour

FIG 11

- In cryogenic air separation, the column is driven not by heat input as in separations above ambient but by work input from the air compressor. An intermediate re-boiler will operate at a lower temperature and require a lower air pressure to drive the system FIG. 12 shows a conventional Linde double column called a conventional cascade and an arrangement of the LP column with an intermediate re-boiler which condenses nitrogen from the top of the HP column called a nested cascade (REF. 9). The bottom re-boiler can operate with partially condensing air. The effect is to reduce the air compressor discharge pressure from 5.7 bar to 4.4 bar. Note that changes in the cycle to improve column efficiency will also improve efficiency in other sections of the plant. The air compressor power is reduced by 15.6%.



	Pressure kPa	psia	Energy
Conv'l	579	84	1.0
NEC	441	64	.844

FIG 12

There are a very large number of cryogenic air separation process cycles described in the patent literature, but they all depend on combinations of the techniques described above. The following sections show a few examples which are suited to the duties and process cycle integrations required for oxyfuel and gasification systems with CO_2 capture and which may be used in future.

3.7.3 Cycles for Oxyfuel Coal Fired Power Generation

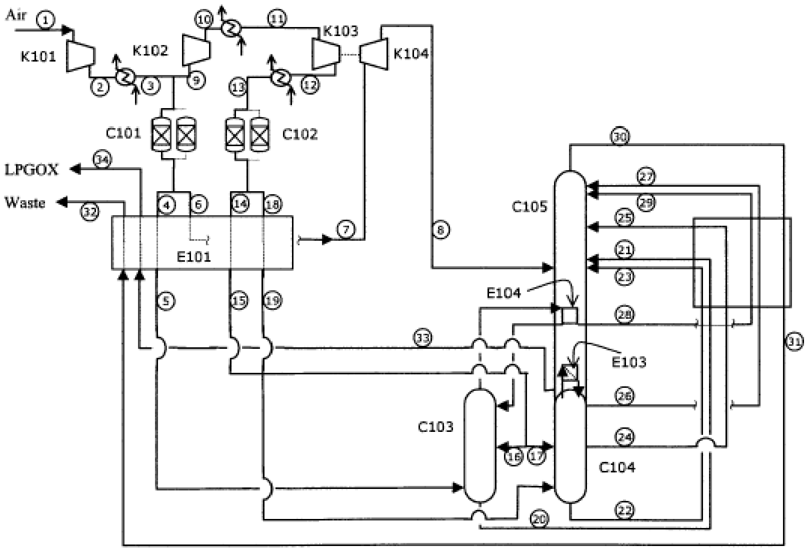


FIG 13

FIG. 13 shows an efficient oxygen plant designed by Air Products for an oxyfuel coal based power generation system (Ref.32). The plant is designed to produce 95% purity gaseous oxygen at 1.6 bar pressure. The column arrangement is a more complex version of the nested cascade (FIG. 12) in which an additional HP column C104 is used. This cycle produces a gaseous oxygen product stream at 1.6 bar by taking a liquid oxygen product flow point 33 from the sump of an LP column C105 which has a pressure of only about 1.45 bar. The oxygen is pressurised by hydrostatic head, and vaporised in the main heat exchanger against a condensing air stream at 5.3 bar leaving at near ambient temperature 34. The main air compressor K101 is an adiabatic axial flow machine with a discharge pressure of 3.5 bar at a temperature of 144°C, point 2. The discharge air stream is reduced in temperature to 12°C, first by pre-heating condensate from the steam turbine condenser prior to de-aeration and secondly by cooling with chilled water from the waste N_2 direct contact water chiller tower (not shown). No cooling water is required during normal operation. The air stream 3 is then divided into two equal parts. The first is purified and dried in the adsorbers C101 before entering the cold-box, while the second 9 is further compressed in two stages to 5.3 bar, purified and dried in the second adsorbers C102 and cooled to ambient temperature before entering the cold box. Part of the lower pressure air stream enters the side column C103 at point 5 together with part of the liquefied portion of the higher pressure air stream. The remaining part 17 of the liquid stream is used as intermediate reflux in C104. The overhead from C103 is a nitrogen rich stream which condenses in the intermediate re-boiler E104 then divides to produce reflux for C103 and an intermediate reflux stream 29 to the LP column C105. The remaining portion of the low pressure air stream 7 is used to provide refrigeration in the turbo expander K104. The remaining part of the higher pressure air stream provides feed to the base of the HP column C104. The turbo expander discharge at point 8 provides a gaseous feed to the LP column C105. The turbo expander K104 is directly coupled to the final booster air compressor wheel K103 to efficiently use the generated shaft power. The HP column top gas condenses in the LP column re-boiler E103 and provides pure liquid nitrogen reflux to the HP column and the LP column 27. In addition to the liquid bottom product from C103 and C104, a liquid air stream is taken from an intermediate point in C104 and all three streams are used as feeds to the mid section of the LP column.

This rather complex cycle has the advantage of a very low power consumption of 201 kWh/tonne O_2 contained. The work efficient LP column has two reflux points, four feed points and an intermediate re-boiler. The use of two high pressure columns reduces the column diameter compared to a single HP column. Each of these two columns could be surmounted by an LP column, allowing column systems for oxygen plants of 7000 to 10,000 tonne/day capacity to be shop fabricated.

There are a number of variations on this cycle which have been considered by the industrial gas companies. In each case there is a combination of one or more intermediate re-boilers with multiple LP column feeds and in some cases a single feed air pressure. The oxygen product can be taken from the LP column as a gas and compressed from near atmospheric pressure to 1.6bar with a single stage oxygen gas compressor.

Future reduction in the specific power consumption of all large cryogenic air separation plants will depend on the development of significantly higher efficiency air and nitrogen compressors. Table 4 gives a typical breakdown for current operating plants designed in the 1970's and 1980's. Current designs might use a main air compressor with an isothermal efficiency of 76%. Use of an axial compressor with compression heat used efficiently in the power cycle is possible in most oxy-fuel cycles. This significantly improves overall efficiency. Gas turbine cycles generally have excess low temperature heat available so this option is not effective. With inter-cooled machines, the use of plate-fin heat exchangers as inter-coolers can reduce approach to cooling water temperature to below $1^{o}C$. Additional lower pressure ratio stages and advanced fluid dynamic design of the compressor stages, both wheels and diffusers, can further increase efficiency. Isothermal efficiencies of 80% are possible with current technology given the incentive to meet the additional capital cost.

3.7.4 Cycles for Coal, Bitumen or Petcoke Fuelled Gasification

Oxygen for fossil fuel derived gasification systems requires pressures currently in the range 40 bar to 80 bar and in the future possibly 100 bar with the development of higher pressure gasifiers. Oxygen purity is typically in the range 90% to 97%. Generally all of the nitrogen produced by the plant can be used for dilution of H_2 in CO_2 capture applications. This is a more efficient option than steam dilution but in some circumstances low temperature level waste heat may be available from the system which can be used for water evaporation to humidify the fuel gas stream. The oxygen content of the diluent N_2 must be kept in the range 1% to 2% to avoid any possible exothermic combustion of the mixed H_2 rich fuel gas. It is essential that the plant design and control system should be carefully reviewed to ensure that both O_2 and N_2 purities can be maintained within specified tolerances during changes in gas turbine loading and unloading for possible power station load following operation.

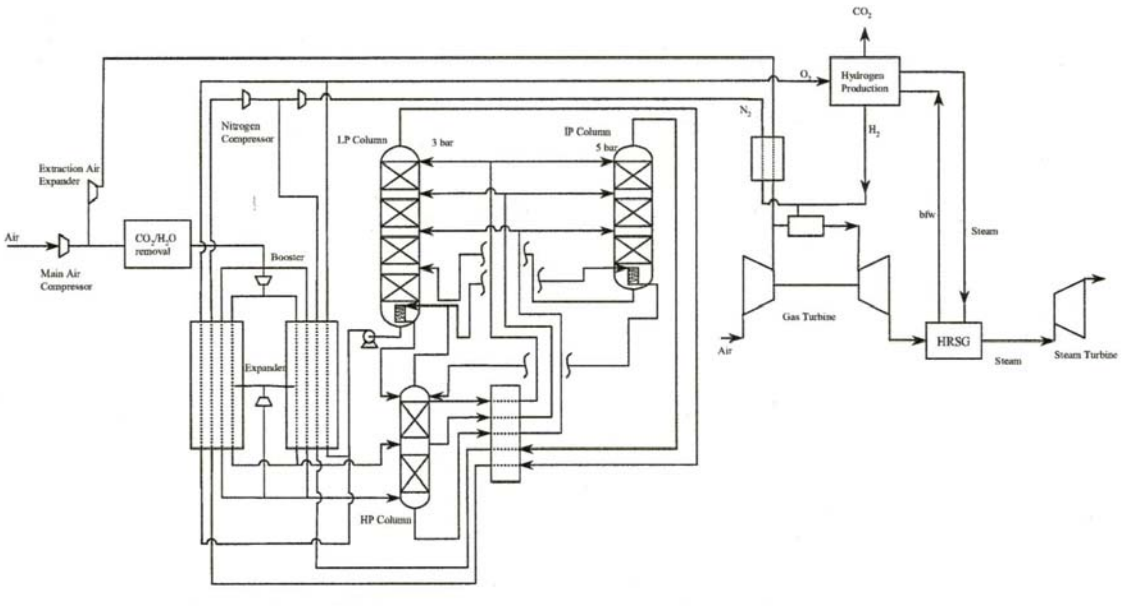


FIG 14

FIG. 14 shows a high efficiency triple column cryogenic air separation plant integrated with a gasification system producing H_2 and with a gas turbine combined cycle power generation system using the hydrogen mixed with nitrogen diluent as fuel. The plant uses an air feed at 10 bar pressure. It has a single high pressure column and two low pressure columns operating at about 3 bar and 5 bar pressures (REF. 10). All the available N_2 from the top of these two LP columns is warmed in the main heat exchanger against cooling feed air and compressed to H_2 fuel gas pressure and used as diluent for the H_2 fuel to load the gas turbine and reduce NOX formation. The flow sheet shows air flow bled from the gas turbine as a partial air feed for the ASU. The gas turbine bleed air is cooled against the compressed N_2 diluent and the excess pressure energy is recovered by expanding the air in the power producing turbine to 10 bar where it mixes with the auxiliary air compressor flow. This expansion turbine effectively de-couples the ASU and the gas turbine allowing the pressures in the ASU to be closely controlled, and product purities to be controlled during load changes. It should be noted that for a system using a GE H frame gas turbine there will be sufficient air flow available to provide 100% of the ASU air requirement and no auxiliary air compressor will be required. This double LP column arrangement allows the O_2 product to be removed from the 3 bar column sump as a liquid, pumped to delivery pressure and vaporised against a condensing high pressure air fraction which has a pressure in the range 60 to 100 bar depending on the oxygen delivery pressure. The condensed high pressure liquid air is used as an intermediate feed to the high pressure column. Both of the low pressure column re-boilers are heated by condensing nitrogen from the top of the high pressure column. The condensed liquid nitrogen provides the reflux flow to the top of all three distillation columns. The composition of the liquid in the sump of the 5 bar column is about 70% O_2

and this is used as an intermediate feed for the 3 bar column so that the composition can be further increased to 95% by distillation in the bottom section of the 3 bar column. This arrangement has the effect of boosting the delivery pressure of a significant fraction of the total nitrogen product from 3 to 5 bar with no increase in the air inlet pressure. If it was possible to use an H frame GE gas turbine with the capability of supplying 100% of the air flow for the ASU, it would be possible to increase the air inlet pressure to perhaps 15 bar. This would give N_2 product delivery pressures from the two LP columns of 5 bar and 8 bar with a small reduction in the oxygen recovery from the system. The combination of high operating pressure in the distillation columns and multiple feed points have moved the operating lines in the column sections close to the equilibrium O_2/N_2 curves which has reduced mixing losses. The effect on other equipment items such as the possible elimination of the air compressor and the reduction in equipment sizes is significant in reducing the capital and operating cost of the system.

All of the major suppliers of cryogenic ASU equipment have produced patented process cycle designs which have the same general characteristics as those outlined in Section 1.7. They all seek to provide low cost O_2 and N_2 for high power cost situations such as carbon capture power generation and H_2 production. To summarise, the features of future large size cryogenic oxygen plants for CO_2 capture applications are:-

- Highest practical distillation column pressures.
- Multiple intermediate re-boiler and condensers in the lower pressure columns.
- Multiple distillation columns
- Multiple column feed points
- Reduced capital cost and power consumption for compression equipment.
- Reduced cost and size of equipment with higher operating pressures.

3.7.5 Operability and Control System Challenges

This section will deal with the main operating and control system requirements for oxyfuel and IGCC CO_2 capture systems.

3.7.5.1 Oxyfuel Operability and Control System

Oxyfuel coal fired power generation can be carried out in a system designed solely for operation with pure oxygen as the oxidant. A cryogenic O_2 plant with electric drive, supplied by a reliable electric power grid as a back-up, would have an availability of greater than 99%. The required shutdown for defrosting and maintenance would be once every four years for perhaps a 10 day period which would coincide with normal annual power station maintenance. Plant start-up following a maintenance shutdown would be speeded up if there were a liquid oxygen storage system which could supply liquid oxygen to the plant rather than relying on refrigeration produced by the plants expansion turbines.

New pulverised coal fired power stations designed for oxy-fuel operation do not need to be equipped with alternative air firing capability. The station can be started from cold by first commissioning the ASU using grid power, then starting the circulation blowers on the boiler and introducing pure O_2 to bring the O_2 concentration in the circulating gas stream up to about 25%. At this point the burners can be ignited and the boiler commissioned by ramping up the coal and O_2 flows together. No provision needs to be made for air back-up because the oxygen plant is a very reliable piece of equipment.

Operation of an oxyfuel system generally requires an ability to ramp the boiler/turbine/generator system at a rate of up to 5% per minute. Experience gained in the industry with advanced computer control systems has demonstrated ramping at up to 2% per minute for the Buggenum IGCC plant in the Netherlands, which has a back-pressurised cryogenic oxygen plant having air supplied at 10 bar pressure from the gas turbine air compressor. An oxyfuel plant with complex column and heat exchanger configuration would require a careful dynamic simulation of the plant and integrated control system to provide a reliable control model. Fortunately, modern dynamic modelling software is available (ASPEN PLUS) which can be used to provide a risk free optimised control solution. The ramping can be assisted by using the liquid oxygen storage with a vaporiser to provide part of the increased oxygen demand as the plant ramps up. As an example, consider a 10000 tonne/day O_2 plant at minimum load of 60% ramping to 100% at 5%/min. If the ASU could only ramp reliably at 2%/min the time taken to reach 100% would be 20 minutes and in this period 16.7 tonnes of liquid oxygen would be vaporised. The ASU could easily be designed with the refrigeration expansion turbines sized to allow say 0.5% of the oxygen product to be produced as liquid oxygen which would be sufficient for three re-ramping operations per day. The power consumption of the plant would increase by about 0.75%. Turn-down of the plant from 100% to 60% load at 5%/min with the ASU ramping at 2% per minute would involve venting 16.7 tonnes of gaseous oxygen.

3.7.5.2 IGCC Operability and Control System

The gasification of a hydrocarbon or carbonaceous fuel for power generation using pure oxygen will usually involve the integration of the cryogenic oxygen plant with the gas turbine. Location of the air separation plant on a separate site with pipeline supplies of O_2 and possibly N_2 is a significant additional expense. If an O_2 pipeline supply were used with only minimal N_2 availability then steam would have to be used for H_2 dilution and the opportunity for maximising gas turbine output by air and nitrogen integration would be lost.

Part or all of the air needed for oxygen production is taken from the discharge of the gas turbine compressor as has been discussed in previous sections. All of the nitrogen will be needed for H_2 dilution with a dedicated power plant. A lower fraction might be needed if part of the gasifier output was used for H_2, chemicals, or Fischer-Tropsch hydrocarbon liquid production.

The start-up of the system requires first the O_2 plant to be commissioned, followed by the gasifier and finally the gas turbine combined cycle power generation system. For this sequence to be used, it must be possible to feed the cryogenic ASU with a minimum of 60% of its maximum air flow requirement. This requirement is not a problem with a partial air feed case. Future gas turbine models such as the GE H frame units will be derived from existing models with steam cooled hot components. This releases air, formally used internally for turbine blade cooling duty, which means that total air feed to the ASU from the gas turbine may be possible with significant saving in power consumption for the ASU. Start-up then becomes a problem of economics. The cost of a standby 60% air compressor must be set against the cost of natural gas or liquid back-up fuel for the gas turbine during start-up periods based on the expected pattern of operation of the IGCC system.

Ramping of the oxygen plant with the IGCC system responding to required load changes will be similar to the considerations outlined for oxyfuel boiler systems. As before, control system dynamics for total plant operation can be studied and optimised at the design stage. The additional constraint on the ASU is that both the O_2 and N_2 purities must be maintained within strict limits for safe operation of the gas turbine fuel supply. A further desirable feature is the option to provide a backup high pressure vaporized O_2 stream which can maintain the O_2 supply pressure to within 1 bar for a few hours in the event of an ASU trip. The availability of the complex gasifier combined cycle power generation system and other downstream equipment can be improved.

3.8 Future development and implementation of cryogenic O_2 systems

Cryogenic air separation is a very mature technology which is practised by a small number of international and Chinese companies in a highly competitive environment. A multi plant facility producing about 20,000 tonne/day O_2 is currently under construction by The Linde Company in Qatar using the latest technology to be used for Fischer–Tropsch liquids production based on natural gas feed. Single train plant sizes of 5000 to 6000 tonne/day O_2 are being offered commercially. Single train axial flow air compressors for a 10000 tonne/day O_2 plant would be larger by a factor of 2 to 3 compared to current demonstrated experience but the technology is well understood by the manufacturers and risks would be low. A 2000 Mw coal fired oxyfuel power station requiring about 40,000 tonne/day O_2 would need 4 oxygen plants which could be supplied now. Complex low power consumption process cycles will be used having multiple columns and re-boiler condenser units. Some of these columns will be shop fabricated and some will be fitted with packing and fluid distributors on site. There will be a need for the industry to significantly increase capacity for the manufacture of aluminium plate-fin heat exchangers and possibly implement improved manufacturing methods including a degree of automation in assembly and the fabrication of larger cross-section blocks. The development of high capacity efficient packed column technology has been a major preoccupation in the past few years and no significant improvement in performance in the future should be expected. The increased column diameters required for larger plants are still well below diameters used in the petrochemical and refining industries. Any further reductions in specific power consumption are likely to be very marginal in view of the highly developed technology for gas compression, process cycle design, heat transfer units and packed distillation systems. Capital costs will be reduced somewhat by the large increase in single train plant size required particularly for future oxy-fuel plants.

The major challenge for the industry will be the huge increase in output of air separation plants required for the implementation of a world-wide programme of CO_2 capture and storage. This will require significant increase in manufacturing capacity for all equipment required for the plants, in engineering resources and in the field of construction services.

The technology of cryogenic air separation is very well suited to the low pressure O_2 requirement for oxy-fuel coal fired power systems which are likely to remain highly competitive to IGCC systems with CO_2 capture in the future. IGCC is more suited to the high temperature O_2 ion transport systems.

4. OXYGEN PRODUCTION USING SOLID ELECTROLYTES

4.1 The Oxygen Transport Process

Certain mixed metallic oxides are capable of conducting oxygen ions through their crystal lattice. Unlike polymeric or porous membranes, these dense materials are 100% selective for oxygen. They are solid electrolytes which will conduct both oxygen ions and electrons under the right operating conditions. In general it is necessary to have a temperature above $600^{o}C$ to achieve high electrical and ionic conductivity.

An ion transport membrane (ITM) will operate either as an electrically driven device or as a concentration cell. An electrically driven device would consist of a high temperature ITM with the two faces connected through a DC power source and supplied with atmospheric pressure air on the cathode side. The oxygen molecules ionise on the cathode surface, and to maintain electrical neutrality in the ITM, simultaneously, oxygen ions give up electrons and leave the ITM from the anode face with the DC power supply acting to drive the electro-chemical process. This device is capable not only of separating oxygen from the atmospheric pressure air but also of delivering the oxygen at an elevated pressure depending on the applied voltage.

If the high temperature ITM is exposed to a difference in activity on its two faces such as a difference in oxygen partial pressure, a concentration cell is set up which has an electromotive force E given by the equation.

$$E = (RT/4F)\ln(P/P_{perm}) \qquad (4.1)$$

Where P and P_{perm} are the upstream and downstream oxygen partial pressures, F is the Faraday constant, R is the gas constant and T is the absolute temperature.

If the solid electrolyte has both ionic and electrical conductivity then it becomes a mixed conductor with electrons and oxygen ions being conducted simultaneously in opposite directions due to this internal short circuiting process. The net result is that when a high temperature mixed conducting ITM is exposed to an oxygen partial pressure difference oxygen diffusion takes place.

The oxygen flux through mixed ionic and electronic conducting ITM membranes can be readily approximated by the equation.

$$J_{02} = -(RT/(16F))\, o_i \ln(P/P_{perm})/L \qquad (4.2)$$

Where L is the membrane thickness, o_i is the ionic conductivity. This equation applies to situations where the rate limiting step to oxygen transport is the solid state diffusion of oxygen anions across the membrane and to the situations when the ionic conductivity is approximately constant between P and P_{perm}. The temperature dependence of the ionic conductivity of a mixed ionic and electronic conductor can be described by an Arrhenius relation:-

$$o_i = o_o \exp(-E_A/RT) \qquad (4.3)$$

Where o_o is a constant and E_A is the activation energy. Therefore, at a given oxygen partial pressure driving force, the oxygen flux will increase exponentially with increasing temperature, in the absence of any other resistances to mass transport. Practical oxygen fluxes can be achieved at temperatures above 750°C, preferably above 800°C.

The major characteristic of high temperature mixed conducting ITM's is their infinite selectivity to the diffusing species, in this case oxygen, and their extremely high permeability. The rate of diffusion in an ITM is proportional to $\ln(P/P_{perm})$ rather than $(P-P_{perm})$ as with a polymeric or conventional porous membrane. As an example a typical polymeric membrane for oxygen diffusion might have a maximum permeability of 100 Barrers at an oxygen to nitrogen selectivity of 6. The typical permeability of current ITM's is in the range of 10^6 to 10^7 Barrers. In practice there may be small defects in the ITM membrane or in the ceramic to metallic seals used in the ITM modules which would cause leaks of nitrogen and argon from the air feed side to the permeate side. Quite significant leakage would be tolerable in a practical gasification application, where 90% to ideally 95% oxygen purity is specified for cryogenic oxygen systems.

4.2 Calculation of Operating Conditions for Oxygen Transport

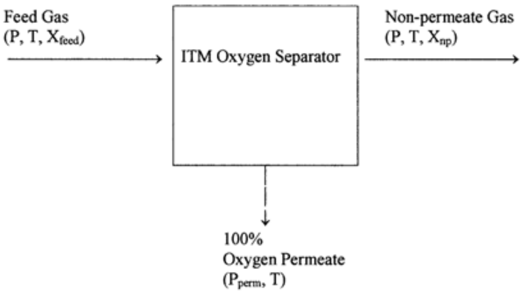


FIG 15

Process calculations can be made from a set of operating equations presented here to describe the situation shown in FIG. 15, in which an oxygen-containing inlet stream of composition, X_{feed}, at absolute pressure, P, passes through a vessel containing one or more ITM devices. Oxygen permeates the device(s) and is collected in the permeate stream at 100% purity and absolute pressure P_{perm}. The oxygen-depleted non-permeate stream passes out of the device at composition, X_{np}, and at essentially unchanged pressure, P. The device(s) operate isothermally at temperature T.

The oxygen-depleted non-permeate gas stream composition can be assumed or calculated from an overall recovery for the process. Recovery, B, is defined as the fraction of oxygen removed from the feed stream as a fraction of that available, or,

$$B = \frac{F_{perm}}{X_{feed}F} \qquad (4.4)$$

Where F_{perm} and F are the molar flow rates of the permeate (oxygen) and feed streams, respectively.

Recovery is ultimately limited by the driving force for oxygen flux. As the feed gas passes across the ITM device, the gas is depleted of oxygen. If the oxygen partial pressure in the gas falls to that in the permeate stream, the net production drops to zero. This point represents the (maximum) Theoretical Recovery point, which can be calculated as:

$$B_T = 1 - \frac{(1 - X_{feed})\ P_{perm}}{X_{feed}\quad (P - P_{perm})} \qquad (4.5)$$

in which B_T is the Theoretical Recovery. Consistent with many industrial separation processes, a commercial ITM separation would be best operated at 50% - 85% of theoretical recovery, depending on the balance between capital cost or membrane area, and energy cost. A useful heuristic for calculating separation performance by ITM is that the oxygen partial pressures in the permeate (product) and feed streams are related by (Based on a recommendation of Air Products).

$$PX_{feed} = \text{(approximately) } 7\ P_{perm} \qquad (4.6)$$

While significant deviation from Eq. (4.6) is possible, it should not be made without a detailed understanding on the ITM process and its economics. Note that P and P_{perm} are absolute pressures.

The non-permeate gas stream composition depends on B according to:

$$X_{np} = \frac{X_{feed}(1 - B)}{(1 - BX_{feed})} \qquad (4.7)$$

Recommended operating temperature, compositions, and pressure are summarized in Table 5 based on current development work with air and air-derived feeds. The ranges depend on the specific application.

Operating Envelope for ITM Oxygen Process Design (Air Products recommendation based on their membranes)

	RECOMMENDED OPERATING RANGE	
Parameter	**Low**	**High**
Temperature , T	800°C	900°C
Feed Pressure, P	6.9 bar	69 bar
Permeate Pressure, P_{perm}	0.13 bar	6.9 bar
Feed oxygen mol fraction, X_{feed}	0.10	0.21

TABLE 5

Equations (4.4), (4.6) and (4.7) can be used to predict the performance of an ITM process to produce oxygen, given the feed composition and desired recovery. Equation (4.5) is used as a guide in the choice of recovery.

As an example, consider a feed stream consisting of 21% (mol.) oxygen at 20 bar pressure flowing at 1,000,000 Nm_3/hr. The ITM product pressure and theoretical recovery can be calculated at 0.6 bar and 88% respectively. Accordingly, the actual recovery is 66% or, from Equation (4.4) with F=1000000Nm_3/hr, the process produces 139,000 Nm_3/hr oxygen. The calculated permeate pressure is within the recommended bounds listed in Table 5.

The oxygen concentration in the oxygen-depleted (non-permeate) stream is calculated at 8.2% (mol.), based on Equation. (4.7).

It should be noted that, in practice, the actual oxygen flux achieved in an ITM module is very considerably less than the values achieved in idealised laboratory experiments. This is due to the diffusional mass transfer resistances which are present on the air feed side and oxygen permeate sides of the membrane. The overall oxygen flux is controlled by the magnitude of these resistances in series. It is essential for the ITM module design to ensure good hydrodynamic conditions which will maximise O_2 flux.

Another method of operating the ITM system is to purge the permeate side of the membrane with an inert gas such as steam, or an oxygen depleted recycle or flue gas. This can be used to produce an oxygen/gas mixture which could be used in a downstream process such as an oxy-fuel combustor, and avoid the necessity of oxygen compression from sub-atmospheric pressure. It is very important to ensure that the impurities present in a possible flue gas recycle were compatible with the chemical constituents of the high temperature membrane used. Dust levels would need to be very low. Possible impurities in coal derived flue gases may rule out this option for coal based systems.

4.3 Application of ITM for Partial Oxidation

The oxygen flux through an ITM is proportional to ln (P/P_{perm}) as shown in equation (4.2). If there is a reducing environment on the downstream side of the membrane, such as a mixture of methane and steam, the equilibrium partial pressure of oxygen will be very low. At the operating temperature of >800°C, the value of P_{perm} for this case is $<10^{-16}$ bar. Under these conditions oxygen diffusion will be very rapid, and conditions will exist on the downstream side for an oxidation reaction to take place. It is possible for oxygen to diffuse from atmospheric pressure air on one side of the ITM to a reaction system at any elevated pressure conceivable on the downstream side. The maximum down stream pressure is only limited by the mechanical strength of the ITM membrane and the ITM module.

There are a number of important features and limitations of this arrangement:-

- The hydrocarbon fuel used on the downstream side of the membrane must be clean and free from impurities which would either coat and block the ITM surface or react with the ITM material. Fuels such as coal or bitumen or petroleum coke would not be feasible fuels. In practice, the only fuels which are satisfactory are natural gas or low molecular weight hydrocarbons. It has been recommended that these feed gases should be preheated with the required proportion of steam and subjected to an adiabatic catalytic pre-reforming step upstream of the ITM to ensure that only methane steam mixture is used as feed gas. (REF. 11).

- It is important that the reactions of the diffusing oxygen with the hydrocarbons or other components do not result in the deposition of solid carbon on the ITM surfaces. The formation of carbon can be inhibited by a small recycle of product gas around the downstream side of the membrane (REF. 12).

- The reactions of hydrocarbons and oxidisable gases with oxygen are exothermic and would result in a rapid temperature rise which would quickly increase the ITM temperature to an unacceptably high level. A partial oxidation reaction with natural gas feed operates with an outlet temperature in the range 1300°C to 1350°C. For acceptable performance there must be a simultaneous endothermic steam/methane reforming reaction which means that the ITM must be used in an arrangement which brings it in contact with a catalyst which is required to ensure acceptable reaction velocity and approach to equilibrium for the steam/methane reaction.

- The design of the ITM module and the actual membrane itself must ensure that the oxygen diffusion rate and the resulting exotherm are balanced by the much slower steam methane catalytic reaction. This is achieved by, for example, coating the ITM with a downstream porous surface to control oxygen diffusion, or controlling the air flow to the upstream side of the membrane or by other means described by a number of patents (REF. 13).

- The very low partial pressure of oxygen on the downstream side compared to the upstream side of the membrane and the very high temperatures imposes an important limitation on the materials which make up the membrane. These are basically mixed oxides (see Section 4.4). The composition and metallic elements chosen must result in a stable composition and crystal structure over the whole range of oxygen partial pressures in the system. There must be zero loss or minimal loss of oxygen by reduction of the oxides on the reducing side of the membrane.

The reactions which could take place are as follows;-

EXOTHERMIC $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
$CO + \frac{1}{2}O_2 \rightarrow CO_2$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$CO + H_2O = H_2 + CO_2$

ENDOTHERMIC $CH_4 + H_2O = CO + 3H_2$
$CH_4 + CO_2 = 2CO + 2H_2$

The most rapid exothermic reaction is the oxidation of the hydrogen which probably results in the bulk of the exothermic heat release.

It is possible to control the reaction conditions so that the inlet gas composition on the fuel or anode side of the membrane and the regulation of feed air on the upstream side of the membrane results in a thermal balance between the endothermic and exothermic reactions. Unfortunately this requires a much higher steam (optionally with some CO_2) to methane ratio than normally used and consequently a lowering of overall thermal efficiency.

As an example the reaction will be isothermal at 800°C 20 bar with a molar ratio of CH_4:H_2O:O_2 of 1:4:0.37 and, at equilibrium the resulting gas composition (reactor exit mol%) would be:-

	Exit Composition	**Dry Basis**
H_2	37	71.0
CO	6	10.9
CO_2	8	14.6
CH_4	2	3.5
H_2O	47	0

A conventional auto-thermal reformer operates with a CH_4:H_2O ratio of between 1:0.6 and 1:1.

Other methods of temperature control for the reactor such as injection of diluents or control of process variables are described (REF. 14).

The alternative is to use a lower ratio and permit a temperature rise which requires a multi-stage ITM reactor system with cooling between stages. The allowable temperature rise per stage depends on the properties of the ITM material but is in the range of 100°C to 200°C.

4.4 Membrane Materials

Most of the references to high performance mixed conducting ITM's refer to perovskite ceramic materials which have a cubic crystal structure over the entire operating temperature range and with compositions which exhibit high oxygen flux (REF. 15). Perovskites with hexagonal crystal structure are not effective for oxygen transport. The perovskite structure must be chemically stable at operating temperatures and gas compositions and it must have good mechanical stability. The formula of typical ITM perovskites is of the form ABO_{3-x} where A is a lanthanide element, atomic number 57 to 71 plus yttrium, B is a transition metal and O is oxygen. The transition metals are those in Period 4 and between groups II and III of the periodic table and include titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc. Other doping elements may be included to enhance stability and performance.

For stoichiometric balance the materials normally have three oxygen atoms, but it has been found that oxygen diffusion rates are increased if there are vacancies in the range 0.05 to 0.5 (the x in the formula ABO_3-x) in the oxygen lattice sites caused by varying the ratio of metallic species in the material. The vacancies are mobile at operating temperature and move throughout the material. Oxygen ions are transported through the material by moving from lattice vacancy to lattice vacancy. By varying the compositions of perovskites it has been possible to obtain structures which are stable at operating temperatures with high and low concentrations of oxygen, carbon dioxide and water vapour and tolerant to the presence of low ppm concentrations of $S0_2$.

There is an extensive patent literature on materials for 0_2 ion transport.

4.5 Membrane Structure

The basic structure of an ITM consists of a very thin dense layer through which the oxygen ion diffusion takes place, backed by a porous support layer which provides the strength for the membrane and through which the oxygen permeate can diffuse. For strength and thermal stability the same perovskite material is generally used for the dense and porous layers.

The geometry of the membrane must be determined based on consideration of amenability to standard mass production based ceramic processing technology taking account of material costs, labour rates and the productivity of the manufacturing process. A second major factor is the stress analysis of the membrane units under design conditions including thermal and pressure cycling during start-up and shutdown. A third important consideration is the problem of providing a reliable connection between the ceramic ITM and the metallic pressure vessels and piping to which the ITM is coupled. The thermal expansion coefficients and thermal conductivities of metals and perovskites are different and seals must be maintained without damage to the membrane over a large number of pressure and temperature cycles between ambient and high operating temperatures and pressures. In order to minimise the number of ceramic to metallic connections the ITM membranes are in general assembled in a geometry which allows a relatively high membrane area to be provided in a ceramic perovskite assembly of membrane elements which make up a membrane module. These modules can then be combined in parallel and fitted with the necessary ceramic to metallic seals to provide a complete ITM unit which is integrated into the oxygen production process.

The design features of each company developing ITM systems are unique and distinctive and are also closely linked to the method chosen for integration of the oxygen production unit and the power system or other systems which it serves. For this reason the subsequent sections of this report will deal with each company’s systems in turn.

4.6. AIR PRODUCTS ITM SYSTEMS

4.6.1 ITM Oxygen Production Systems

4.6.1.1 The Design and Production of the ITM Modules

Air Products has developed a perovskite material for oxygen production with the necessary properties of high oxygen flux and mechanical strength which is amenable to high volume manufacture (REF. 16).

The ITM membrane is fabricated as a planar supported structure as shown in FIG. 16 (REF. 11).

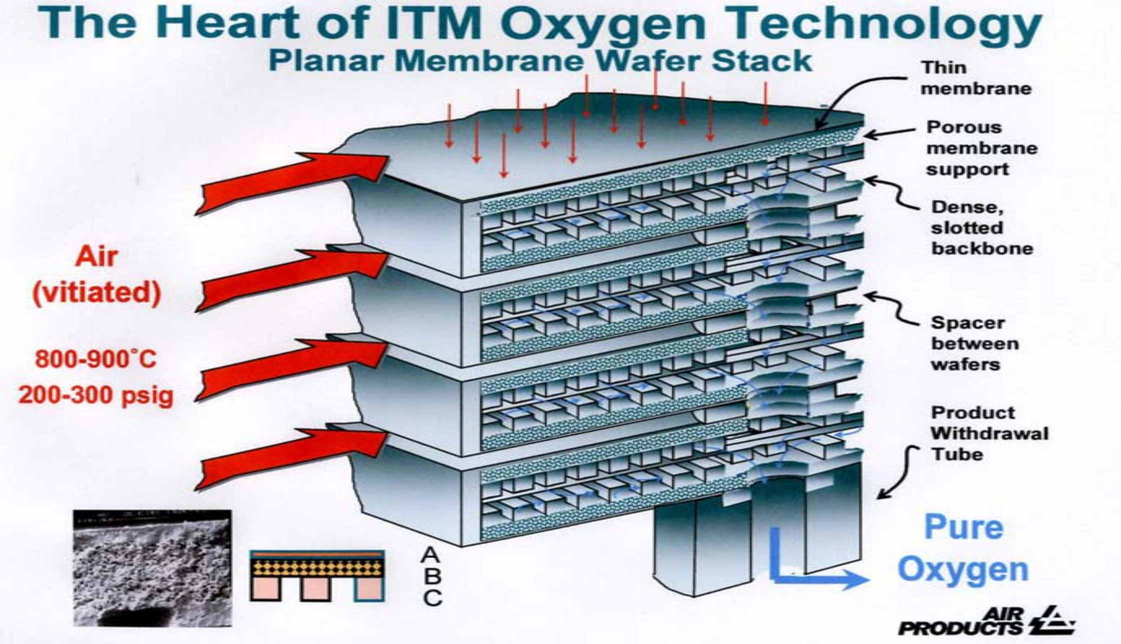


FIG 16

The basic component is a square wafer with two separate ITM membrane faces over which the high temperature pressurised air flows and a hollow centre into which the oxygen permeate, diffuses and collects. Each of the two separate membrane faces are made up of three laminated layers. Firstly a thin outer dense diffusion layer A backed by a thicker porous layer B and then a slotted dense backbone layer C which provides strength and flow passages for the oxygen permeate. These two ITM faces are bonded and edge sealed and have a central hole towards which the oxygen flows. The wafers are stacked between hollow ring spacers forming a central collector tube and the whole assembly is then bonded at high temperature. For convenience a complete ITM module made up of a number of finned tube sections ceramically bonded is assembled and sealed at one end and fitted with a ceramic to metallic connector at the open end as shown in FIG. 17. A typical production ITM module tube would supply about 1 tonne/day O_2. The module, which looks exactly like a section of square finned heat exchanger tube, is assembled in a close packed arrangement in a cylindrical pressure vessel as shown in FIG. 18.

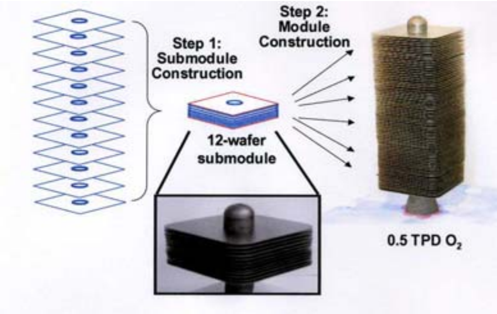


FIG 17

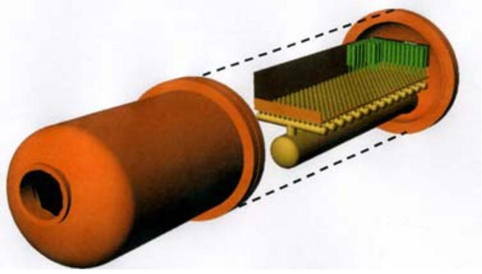


FIG18

The hot high pressure air flows through the pressure vessel over the close packed ITM wafers in an even and uniform regime which minimises mass transfer resistance and maximises O_2 diffusion. The oxygen product gas is collected and piped away in the manifolds shown in FIG. 18. It will be possible to construct 1000 to 2000 tonne/day oxygen production units in easily transportable pressure vessels.

The planar geometry has many advantages over conventional tubes. The ITM surface area per unit volume of pressure vessel is far higher. The number of ceramic to metallic connections is significantly reduced. The mass transfer coefficient on the air side is uniform over the whole fin surface unlike a tube which has a region of low mass transfer on the down stream face (FIG. 19).

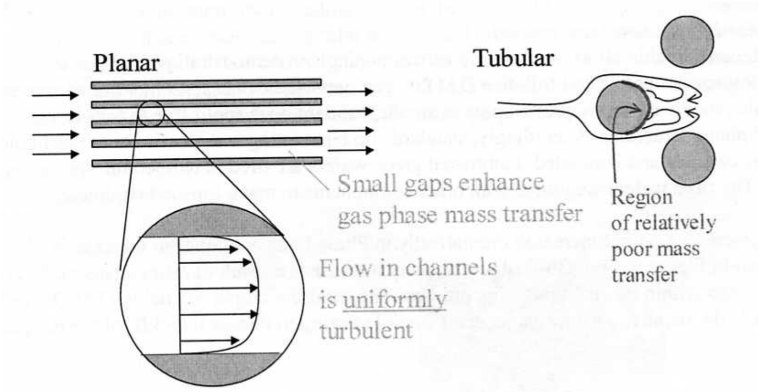


FIG 19

The tubular geometry with only very small variation in wall thickness will generally fail after <1000 hrs operation due to deformation caused by creep at working conditions. In contrast planer modules have high resistance to creep deformation. The maximum stress on the wafer is caused by flow induced vibrations but its design ensures it will survive these fatigue stresses.

The development programme, which was commenced in 1996 has reached the point where 1 to 5 tonne/day 0_2 subscale engineering prototype facility was commissioned in 2005 to operate with full size modules in an identical air flow, temperature and pressure regime to the full size production units (FIG. 20).

FIG 20

These tests have been successful. Target production rates have been achieved, and testing continues. Air Products goal is to supply a large scale O_2 plant to serve the needs of the US FUTUREGEN project which has a projected 2012 start-up date (REF. 17). This will require an oxygen production rate of over 2000 tonne/day.

4.6.1.2 Integration of ITM O_2 Units for IGCC Power Production

The most important application for ITM oxygen systems is to provide O_2 for gasification of fossil derived fuels used in advanced power generation facilities. The basic requirement of an ITM for O_2

production is a source of high temperature high pressure air. This is best provided by integrating the ITM with a gas turbine, which produces adiabatically compressed air at typical pressures of 15 to 25 bar in industrial heavy duty units. The gas turbine is fitted with a second fuel gas combustor which heats part or all of the compressor discharge air flow to 800°C to 900°C before it is passed through the ITM unit as shown in FIG. 21.

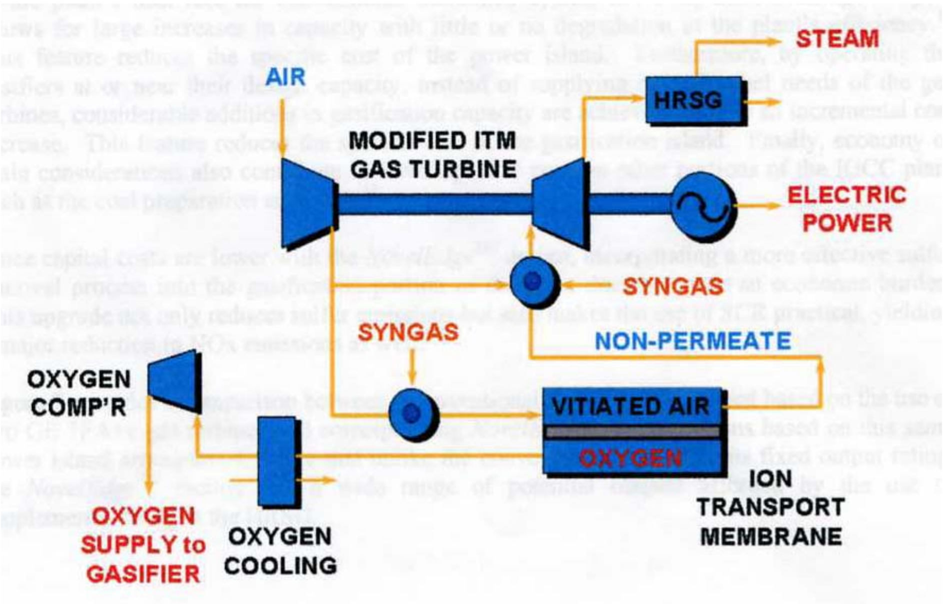


FIG 21

A portion of the air from the gas turbine compressor section is heated by direct combustion of a fuel gas from a gasifier fed with a fossil fuel which has been partially oxidised using oxygen from the ITM unit. The ITM perovskite material will not be affected by the CO_2 and H_2O vapour combustion products present in the air stream. The depleted air stream leaving the ITM unit at 800°C to 900°C still has sufficient O_2 content, to be heated by direct combustion of more fuel gas to a temperature of 1200°C to 1450°C before entering the expander section of the gas turbine, (REF. 18).

The characteristics of this integration scheme include:-

- There is a close integration with the gas turbine which must be capable of providing the necessary air flow for oxygen production as defined in Section 4.2. Based on a 66% 0_2 recovery given in the example, the oxygen flow required for different gasifiers can be compared with the maximum air which can be extracted from the gas turbine. Most gas turbines have limited air extraction capability. The amount of air required for production of the O_2 used by a GE/Texaco quench gasifier producing all its syn-gas flow for gas turbine fuel would be about 25% to 30% of the total gas turbine air flow.

- This limitation on available air extraction rates is particularly relevant to current gas turbine designs which have compact combustion chambers arranged annularly around the periphery of the engine. Some of the earlier gas turbines such as the Siemens V94.2 had large external combustion chambers. In theory the whole gas turbine air flow is available as ITM feed. When turbine air flow is very limited a separate air compressor must be provided in parallel with the gas turbine air compressor section. This situation can be aggravated by the location of the IGCC plant in a higher temperature, elevated location, which leads to a deficiency of air in the gas turbine expander. In this case, loading the turbine section fully will have a beneficial effect on both the power output and the efficiency.

- The use of two combustion systems means that the temperatures of the ITM unit and the gas turbine expander inlet can be separately optimised and controlled.

- An important design feature of an IGCC system is that the H_2 or (H_2 + CO) fuel gas has a higher stoichiometric adiabatic combustion temperature than natural gas, which means that a diluent such as nitrogen (if a cryogenic O_2 plant were used) or steam must be used to lower the combustion temperature and reduce NOX formation. A second important reason for adding a diluent is to ensure the gas turbine expander is fully loaded. When using an ITM O_2 unit, the depleted air stream, with some of its O_2 removed, already contains the diluent nitrogen associated with that oxygen. An amount of extra air flow provided from an external source can be specified to ensure full loading of the gas turbine expander.

A study of a system using a separate air compressor designed for integration with any gas turbine capable of burning H_2 or (H_2 + CO) fuel gas (REF. 19) is presented in Table 6. The study compared a conventional IGCC unit of 543 MW nett output based on coal feed and a cryogenic ASU with the ITM process described. The net power increased from 543 MW to 627 MW and capital cost was reduced from 1500$/kW to 1368 $/kW using the same gas turbines. The efficiency of the overall IGCC power system was 1.2 per centage points higher (41% to 42.2%) for the ITM than the cryogenic ASU case. Another process called "Novel Edge IGCC" shown in REF. 19 describes a method of eliminating the direct fired ITM air pre-heater and using the gas turbine exhaust which is heated from its normal temperature of about 600°C by duct firing H_2 or (H_2+CO) so that its temperature is raised sufficiently to heat the ITM feed air stream to the required operating temperature of 800°C to 900°C. This also has the effect of raising the partial pressure of oxygen in the ITM air feed since no oxygen is consumed for direct fuel burning in the ITM feed stream. The extra fuel that was used for duct firing results in a large power increase from the steam turbine system. The results of all the cases considered in REF.19 based on a single coal slurry feed gasifier of variable size but with the same gas turbine in each case is shown in Table 6. The combination of all features is claimed to result in significant reduction in both capital and total operating cost.

Plant Configuration	**Power Output (MW)**	**Capital Cost ($/kW)**	**Fuel Cost ($/kWh**	**Capital Cost ($/kWh)**	**O&M Cost ($/kWh)**	**Total COE ($/kWh)**
Conventional IGCC cryo ASU	543	1500	.0133	.0214	.0110	**.0457**
Conventional IGCC with ITM Oxygen	627	1368	.0132	.0195	.0098	**.0425**
NovelEdge™ IGCC with cryo ASU	785	1305	.0131	.0186	.0088	**.0405**
NovelEdge™ with ITM Oxygen	820	1224	.0126	.0175	.0083	**.0383**

Based on $1.50 per MMBtu for fuel and 80% capacity factor.

TABLE 6

The use of CO_2 capture with IGCC power production does not affect the integration of ITM oxygen production with the gas turbine when using current chemical or physical absorption systems such as amines, Selexol or Rectisol processes.

4.6.1.3 Integration of ITM O_2 Units for Oxyfuel Power Production

A major application for oxyfuel CO_2 capture processes is the combustion of coal or other fossil derived fuels in conventional power boilers or heaters operating at atmospheric pressure. The oxygen delivery pressure required for a large pulverised coal fired boiler is about 1.7 bar abs. There is no source of high pressure air for ITM feed so a separate air compressor would be required with air feed preheated against depleted air from the ITM unit and in the boiler convection section. The depleted air would be expanded to recover useful power to help drive the air compressor. The arrangement described is essentially a gas turbine, and the most efficient method of using ITM O_2 with an oxyfuel system is to integrate an ITM coupled to a gas turbine with the oxyfuel combustor. In order to maximise system efficiency, and CO_2 capture it would be necessary to provide the gas turbine fuel as H_2 gas derived from a pre-combustion decarbonisation process. All of the gas turbine air flow would ideally be used as feed to the ITM module in order to maximise O_2 production and this would provide a significant fraction of the O_2 required for the oxy-fuel boiler. A study on oxyfuel conversion of refinery process equipment (REF 20) compared such a system using Siemens V94.2 and V94.3 gas turbines with gas turbine fuel to one using a conventional oxyfuel system with cryogenic O_2. The gas turbines were assumed to be fitted with external combustors so that all of the compressor air was extracted and processed in the ITM units producing O_2 in excess of that required for the gasification units which could be made available for the oxy-fuel combustion.

The cases considered showed a variation from 38.9 to 43.2 \$/tonne CO_2 avoided for the cryogenic O_2 cases and from 20 to 38.1 \$/tonne CO_2 avoided for the ITM cases. The main difference was the very large excess natural gas fuel impact for the gas turbines for the ITM cases and the large additional power output from the gas turbines. The value of input natural gas and export power roughly balanced for the cases considered.

It is useful to consider the integration of an oxyfuel pulverised coal fired power boiler and a gas turbine system for future power production with CO_2 capture. The gas turbine would use an ITM module processing all of the compressor air. Gas turbine fuel would be produced by coal gasification. The O_2 production would not only supply the gasifier requirements but also a significant proportion of the oxy-fuel system O_2 demand depending on the relative capacity of the gas turbine and the boiler. The two units would use a common steam turbine system and low level heat recovered from the coal gasifiers would be used for condensate and boiler feed-water preheating. The units would share facilities for coal importation and handling and cooling water and other services. Such an arrangement could be used for new plants or re-powering existing boilers. Gas turbine manufacturers may be encouraged to produce high efficiency units with the option of external combustors allowing 100% of the gas turbine air to be used in the ITM units.

4.6.1.4 Summary

Table 7 summarises the results of Air Products studies on a number of processes using large quantities of O_2 comparing the ITM and cryogenic systems. ITM oxygen results in very large cost savings.

APPLICATION	PRODUCT		SAVINGS (% of Cryo ASU)	
	OXYGEN Tonne/day and bar	POWER (MW)	CAPITAL FOR OXYGEN	POWER FOR OXYGEN
IGCC	2900/78.5	458	35%	37%
Decarbonised Fuel	2180/79.3	300	35%	36%
Enrichment	1360/14.8	260	27%	69%
Oxyfuel/refinery application	7280/1.7	500	48%	68%
GTL	11340/42.4	n/a	20+%	n/a

TABLE 7

4.6.2 ITM Syn-gas (H_2 + CO) Production Systems

4.6.2.1 The ITM Syngas Modules

Air Products chose to design its ITM syngas production system in a planar wafer configuration which consists of a stack of wafer units mounted on a central gas distribution core structure with provision for even shell side flow over the close packed wafer surfaces (FIG. 22). The design philosophy is similar to the configuration described in section 4.5 for the oxygen membranes. The stacked wafer assemblies are then located in a cylindrical pressure vessel with a single axial shell side flow path. One of the most important mechanical design features of this arrangement of membrane surface is that the low pressure area of the membrane must be between the two external faces of the membrane and that the high pressure area should be external. For syn-gas generation this means that the lower pressure air feed should be on the inside of the membrane with the higher pressure natural gas/steam feed and syn-gas generation on the outside surface, on the pressure shell side.

The membrane material is composed of a perovskite with formula $(La_{1-x}Ca_x)yFeO_{3-Z}$ (REF. 21) which has been developed to achieve the required O_2 flux, strength and stability at the operating temperatures and oxygen partial pressures experienced in this system, with oxidising conditions on one side of the membrane and reducing conditions on the other. The inner surface of the membrane, which is exposed to the feed air flow, has a thin dense active layer which is backed by a porous support layer on the shell side which, in this case, is manufactured with an inner structure that inhibits oxygen diffusion. The outer part of the porous layer is impregnated with an active steam/methane reforming catalyst.

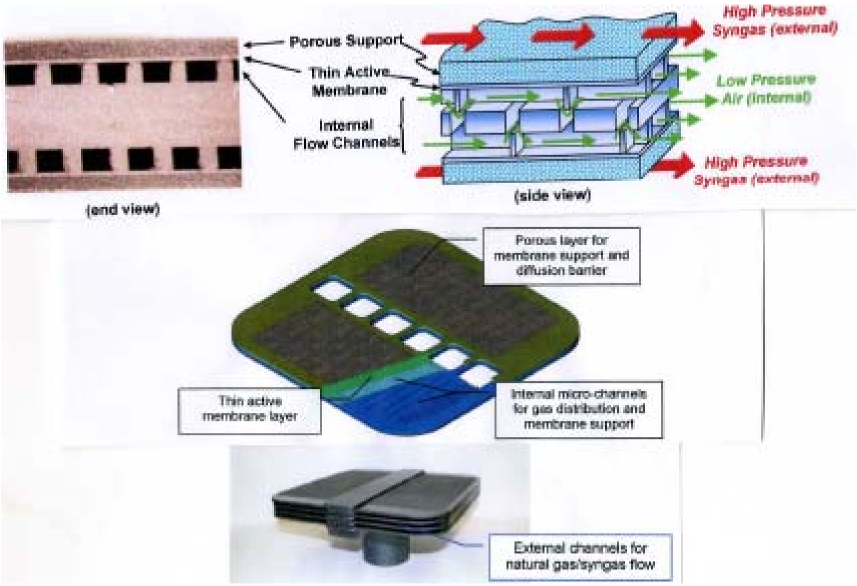
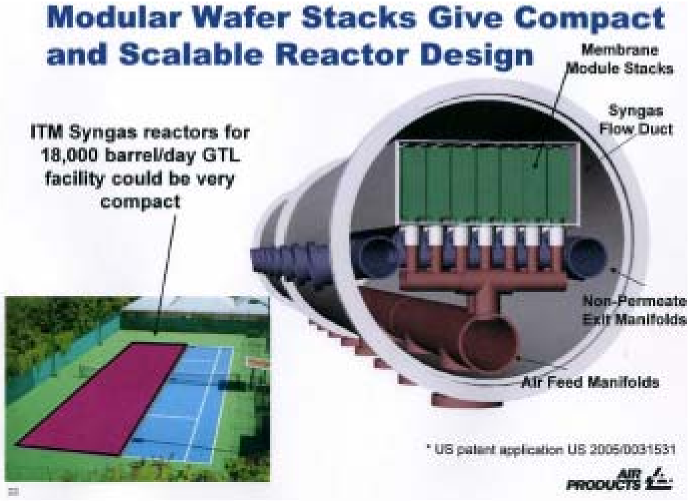


FIG. 22

The specification of this composite layering of the membrane ensures a thermal balance between the endothermic reforming reactions on the shell side and the exothermic oxidation reactions caused by the diffusing oxygen. Internal supports reinforce the membrane wafer structure to withstand the external compressive forces. The configuration of these internal support ribs directs the air flow in a circulatory pattern around the whole internal surface area from the central air entry ports to the central air exit ports. Each wafer is separated from the next by a perforated spacer as shown and the stack of wafers is ceramically bonded to form a module with the necessary inlet and outlet connections. The design of the wafers is amenable to standard ceramic fabrication procedures. An important feature of the design is the use of the same perovskite material throughout the membrane module assembly. (REF. 22).

This complex design has been under development since 1999 and has resulted in a 300 fold increase in module area. The design has been tested at full scale commercial module size in a process development unit with a capacity of about 30 Nm^3/hr (H_2 + CO) gas flow. Several six month endurance tests have been successfully carried out. These have demonstrated design capacity and target oxygen flux rates and leak rates. The modules have been successfully tested under changing operating conditions. The assembled membrane modules are arranged in a pressure vessel as shown in FIG. 23 (REF. 23). Note the area required compared to the size of a tennis court.



Modular Wafer Stacks Give Compact and Scalable Reactor Design

ITM Syngas reactors for 18,000 barrel/day GTL facility could be very compact

Fig 23

The low pressure air feed and non-permeate exit manifolds are connected to multiple exit nozzles on the vessel shell to minimise pressure drop. The membrane modules are surrounded by a syn-gas flow duct which ensures even flow conditions and good mass transfer and heat transfer for the oxidation and reforming reactions to take place. The approximate area to accommodate the syn-gas reactor for the production of 600,000 Nm^3/hr syn-gas is also shown.

The timing of the development programme calls for a prototype facility of about 1100 Nm^3/hr syn-gas flow rate by 2008 to 2010 and a commercial scale plant in the range 22000 Nm^3/hr to 170000 Nm^3/hr of syn-gas by 2010 to 2012. The original target market is the conversion of remote natural gas to Fischer-Tropsch liquids. The plant range would be capable of providing the 2:1 ratio H_2:CO syn-gas for an 800 to 5000 barrel per day FT liquids production. The system would be ideal for the production of H2 with CO_2 capture.

4.6.2.2 Integration of the ITM into a (H_2+CO) Production Plant

Air Products proposes to produce the (H_2+CO) syn-gas for a Fischer-Tropsch liquid hydrocarbon synthesis plant based on natural gas feed using the ITM syn-gas unit as part of the integrated system. The flow sheet is shown in FIG. 24. Natural gas is heated, de-sulphurised and blended with steam and any recycle off gas from the FT reactors. The gases are further heated to about 550°C and passed through an adiabatic pre-reformer where some H_2+CO is formed and where higher molecular weight hydrocarbons are reduced by hydro-cracking to methane. The steam/methane mixture is then reheated to about 550°C and passed into the ITM syn-gas generation unit.

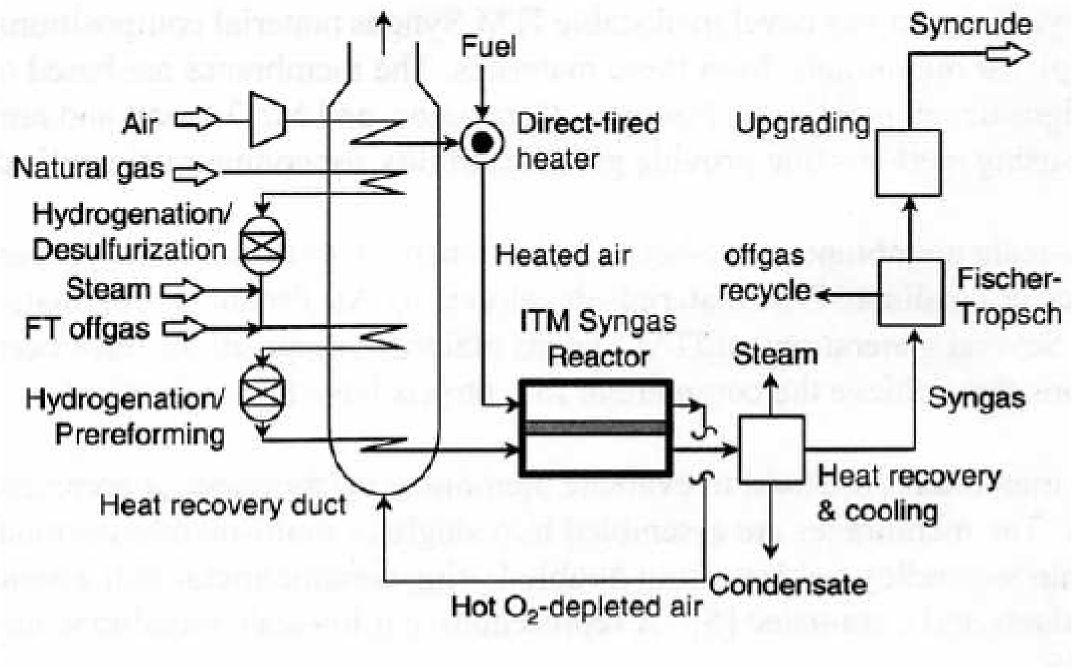


FIG 24

The air-feed to the ITM is compressed to a pressure which will overcome pressure drop in the system and then heated to between 800°C and 900°C firstly in the heat recovery ducted heat exchanger and secondly by the direct combustion of fuel gas in an integral burner unit. The non-permeate stream at 800°C to 900°C leaving the ITM unit is passed through the heat recovery ducted heat exchanger before being vented to atmosphere . Downstream of the ITM syn-gas unit the rest of the plant is conventional with a waste heat boiler heat recovery, gas cooling, water condensation and separation and the FT plant with product upgrading.

The target for this overall system is to achieve greater than 30% reduction in the capital cost of syn-gas generation which, in the case of an FT liquids plant represents approximately a 15% reduction in the overall plant cost.

The thermal efficiency of the overall FT plant using ITM syn-gas production technology is about the same as the current system which uses a cryogenic air separation plant for oxygen production and an auto-thermal reformer for synthesis gas generation. The ITM syn-gas production system can also be used to produce very large volumes of H_2 gas with CO_2 capture for power production or vehicle fuelling. This technology will be used with a different process arrangement in this case to avoid emissions of CO_2. The feed fuel will be natural gas.

4.7 NORSK-HYDRO ITM SYSTEMS

4.7.1 The Advanced Zero Emission Power Plant (AZEP)

The Norsk Hydro development project for an advanced oxygen production system using a mixed conducting membrane is based on the concept of replacing the combustor of a conventional air cycle gas turbine with a novel oxyfuel combustion system (MCM). In order to understand the MCM module design it is necessary to start with an appreciation of the AZEP process which is shown in FIG. 25.

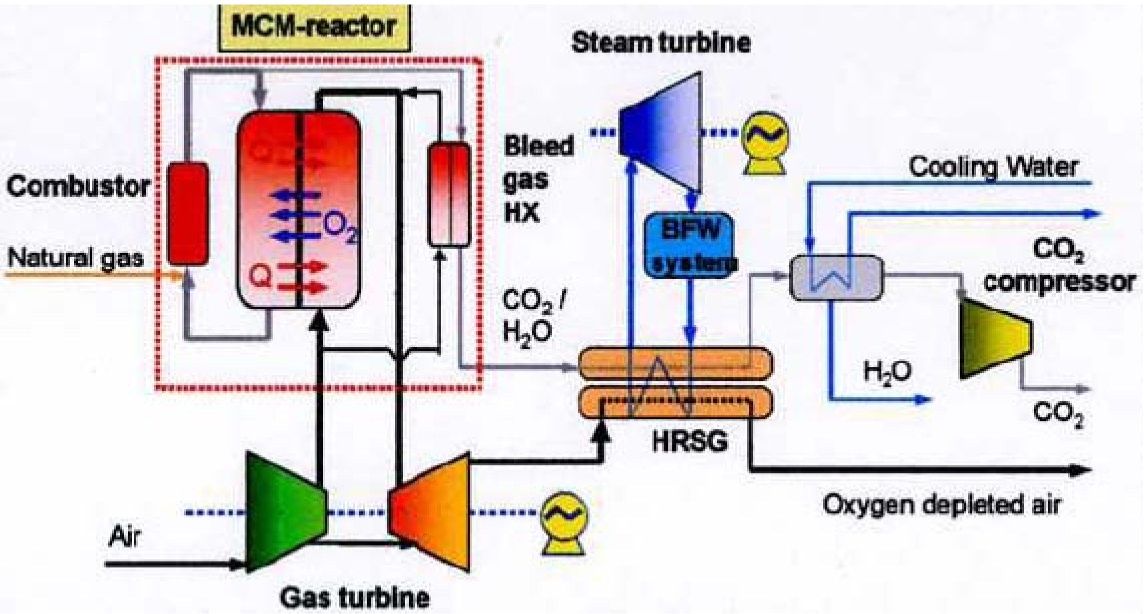


FIG 25

The AZEP combustor is designed to operate with a clean natural gas fuel burning in pure oxygen which permeates through the ITM into the recycled combustion product gas which consists of CO_2, H_2O and a little excess O_2. The combustion temperature is controlled by the recycle ratio. FIG 26 shows the configuration of the membrane module which is sandwiched between two heat exchanger modules, a low temperature module and a high temperature module. The objective of this system is to heat air from the compressor section of the gas turbine in a three stage operation to the required gas turbine expander inlet temperature of about 1250°C. The air is heated to 1250^0C against the oxyfuel combustion gas which enters the high temperature heat exchanger at 1300°C and cools to 1050°C before entering the ITM second heat exchanger. Here the oxygen permeation takes place from the air side into the sweep gas raising the oxygen partial pressure to a level of about 10% sufficient for combustion of natural gas in the external combustor. Simultaneously heat transfer takes place, heating the air from 900°C to 1000°C while the sweep gas cools from 1050°C to 950°C. The third heat exchanger preheats the air from the gas turbine compressor exit temperature of 400°C to 900°C. The cooled combustion product gas is re-circulated using a fan with the flow controlled to maintain the high temperature combustion product gas at 1300°C. The circulating combustion gas and the air stream are at approximately the same pressure. The product of combustion containing CO_2, H_2O and a small fraction of excess oxygen is cooled progressively to recover useful heat as product steam, compressed, dried and purified (depending on CO_2 purity constraints) and delivered at pipeline pressure. As an alternative to heat recovery from the pressurized net combustion gas product, it can be expanded in a power producing turbine to near atmospheric pressure followed by heat recovery into the steam system, water condensation and compression/purification of the CO_2 product.

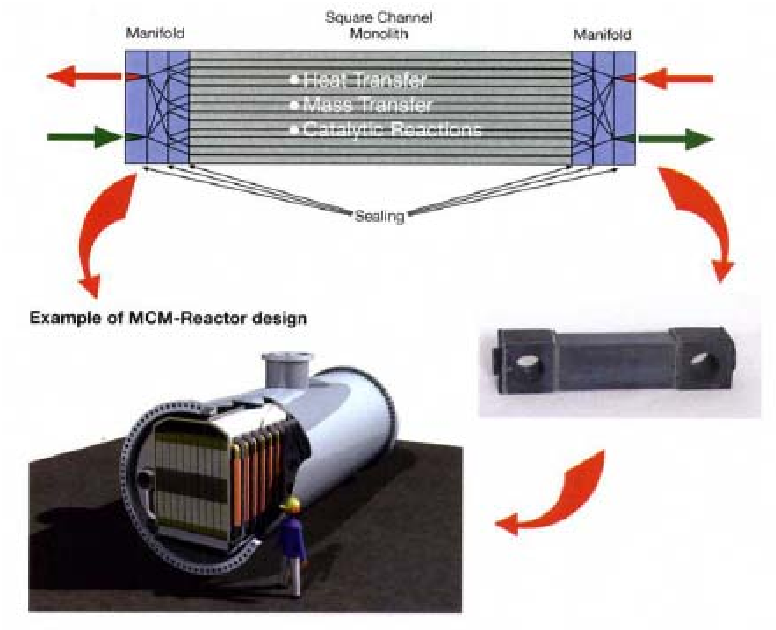


FIG 26

This system offers the potential for higher efficiencies than the pre-combustion decarbonisation of natural gas to produce hydrogen as gas turbine fuel. It avoids the high parasitic power consumption of a cryogenic oxygen plant, the inefficiencies in the conversion of natural gas to hydrogen and also avoids the CO_2 removal step in the process. The efficiency of natural gas combustion for heating the gas turbine expander inlet gas is virtually the same for the MCM reactor/heat exchange module as it would be in a conventional gas turbine combustor. If the high temperature ceramic heat exchanger section can operate reliably in the 1200°C to 1300°C range then the turbine inlet temperature of 1250°C will ensure that there is no significant degradation in gas turbine efficiency. It will be advantageous to include a direct fired air combustor to boost the temperature to the maximum design value for the gas turbine expander inlet if this temperature exceeds the maximum exit temperature from the MCM.

This leaves the normal penalty for CO_2 capture of about 4.5 percentage points which gives a potential efficiency for the system in a combined cycle made of between 50% and 52% (LHV). At present the reported maximum air outlet temperature from the MCM is 12OO°C so there will be a further efficiency loss (REF 23). An analysis based on a comparison with Siemens V94.3 air cycle gas turbine shows an efficiency of 49.6% for AZEP and 57.9% for the V94.3. The breakdown is 4.5 percentage points for CO_2.capture and 3.8 percentage points due to the lower achievable temperature for the expander inlet temperature. A further advantage of the AZEP process is that it can achieve virtually 100% CO_2 capture from a natural gas fuel. The cost of electricity with CO_2 capture and compression using the AZEP process is predicted to be 20% to 28% higher than a conventional natural gas fired combined cycle system.

4.7.1.1 Design and Performance of the MCM Reactor

The basic shape and configuration of the MCM reactor components is shown in FIG 26 (REF. 24). The modules currently produced for testing are 70 mm square by 170 mm long with a 24 x 24 pattern of 2.2 mm width channels separated by 0.5 mm thick walls, coated with a 50 micron layer of dense membrane. The effective membrane area is $540 m^2/m^3$ of MCM volume.

The central O_2 ion transport reactor and the two heat exchanger sections are identical square cross-section extruded ceramic monoliths with a checker board arrangement of passages. They are formed using mixed metallic oxide powders whose properties are selected to suit the required performance criteria of O_2 transport, thermal stability, chemical stability, mechanical properties and corrosion resistance all at temperatures up to 1300°C. The O_2 ion transport reactor is fabricated with a porous ceramic structure. The dense oxygen ion mixed conducting layer is formed by dip coating one section of passages and sintering the monolith to bond the layer in pace. The gas distributors and manifolds are bonded to the ends of the monolith as shown in FIG. 26 using standard ceramic fabrication procedures with particular care to ensure matching of thermal expansion properties to minimise temperature induced stresses in the assembly. The monoliths will be stacked and headered and assembled in the MCM reactor shell as shown in FIG. 26.

Tests on the MCM reactor test section has been carried out in a test cell capable of achieving air and sweep gas temperatures of 1100°C at pressures up to 30 bar (REF. 25). The tests have measured performance in the oxygen diffusion and the lower temperature heat exchange modes required in the MCM module. No testing under conditions required by the high temperature heat exchange has been reported. The maximum temperature attained in these tests was 850°C. Oxygen flux was reported as

2.8 ml/min/cm^2 membrane area with 28% O_2 gas at 10 bar on one side and a CO_2/steam sweep gas on the O_2 permeate side. This is equivalent to a thermal heat release in the MCM module of 15 MW/m^3 of block volume given claimed improvements in the module. The heat transfer performance was equivalent to 100 watts/m^2/^{o}K which meets targets. An industrial gas turbine of 250 MW output at 37% efficiency (LHV) would require an MCM module with a volume of 45 m^3.

The AZEP development programme is now proceeding with scale-up and manufacturing procedures for larger elements and improvements in module performance. No timescale has been given.

4.7.2 Application to Oxyfuel Systems

The concept of operating a gas turbine cycle with CO_2 as the working fluid has been studied by a number of people. A recent study by Alstom (REF. 3) compares a natural gas fired combined cycle power generation using a conventional air cycle gas turbine with CO_2 vented to atmosphere in the exhaust gas with a cycle in which the natural gas is burned in pure oxygen diluted with recycled CO_2 which is the working fluid in the gas turbine. The exhaust gas leaving the heat recovery steam generator (FIG. 4) is cooled to condense excess water vapour. The net CO_2 product of combustion is removed for compression, purification and pipeline delivery and the bulk of the CO_2 is recycled to the compressor section. The efficiency with CO_2 capture is 44.7% (LHV) compared to 56% for the air case and the cost of electricity generated has increased from 3.55 US cents/kWh to 6.13, an increase of 73%.

Norsk Hydro has proposed to replace the cryogenic oxygen plant in the previous example with a mixed conducting ion transport membrane system combustor which is fed with a hot near atmospheric pressure air stream (REF. 26) FIG. 27. The system uses an ITM module to combust a fuel gas in recycled CO_2 rich gas and diffusing O_2. The gas turbine units 3 and 4 operate with a recycle CO_2 stream rather than air. The compressed CO_2 stream 25 leaving the compressor section 4 is preheated in economiser 7 against gas turbine exhaust 19, mixed with fuel gas 16, and enters the ITM O_2 combustor 5. A separate air blower circulates air through an economising heat exchanger 6 which preheats the air before entering the ion transport membrane combustor. Oxygen diffuses into the higher pressure circulating gas stream 17 to combust the major part of the fuel gas and raises the combustion gas temperature to 1000 to 1300^{o}C. The hot combustion gas 18 is expanded in 4 and cooled to near atmospheric temperature in the economiser 7, the steam raising plant and cooling water heat exchangers 9, with condensation of water 21. The CO_2 divides into the net product 23 and the recycle stream 24.

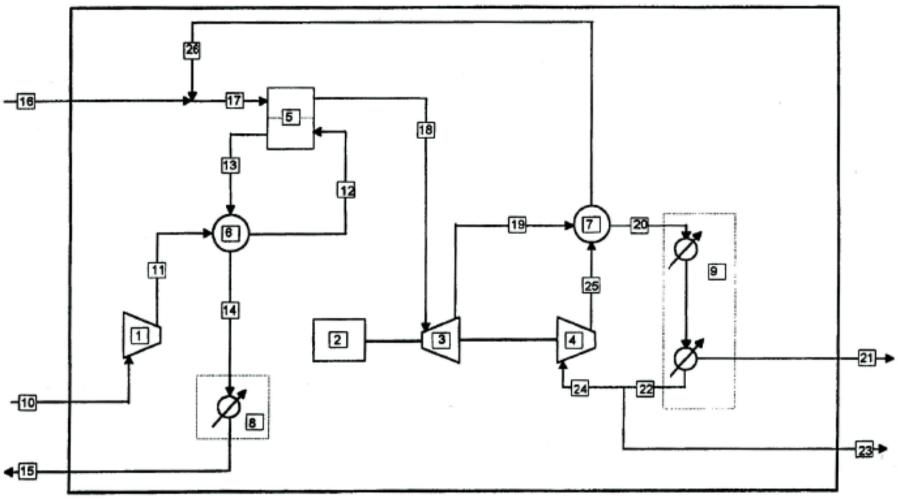


FIG 27

This patent does not give any details of the O_2 ion transport combustor which would need an exit temperature of 1300°C to match the projected performance of the Alstom system with a cryogenic ASU. However, with the Alstrom system the oxygen plant power is 70 MW and the capital cost is 26% of the total power station cost. While it may not be possible to reach 1300°C in an ion transport combustor, lower exit temperatures and lower efficiency will still give potential savings compared to cryogenic oxygen. Further development of this system, which potentially could use similar modules to the MCM system is warranted.

4.8 PRAXAIR OTM SYSTEM

4.8.1 The Configuration of the OTM

The Praxair oxygen transport membrane (OTM) is based on the use of mixed conducting oxygen ion membranes in the form of closed ended tubes sealed at the open end into a metallic tube sheet by means of a coupling and with free floating upper ends (REF. 27). This arrangement has a membrane packing density in the range 100 to 200 m^2/m^3. The higher values are obtained at the expanse of smaller diameter tubes with more ceramic to metallic seals. The tubes can be manufactured in lengths exceeding 1.5 metres. The oxygen permeates from the shell side into the tube (FIG. 28). The tube sheet joints are kept at a lower temperature, below 300°C, to allow simple low leakage low cost jointing of the tubes to the tube sheet. This is accomplished by dividing the OTM reactor into two sections, a lower heat exchange section and an upper oxygen membrane section. The closed ended tubes are free to expand upwards. The baffled shell side provides a cross flow path.

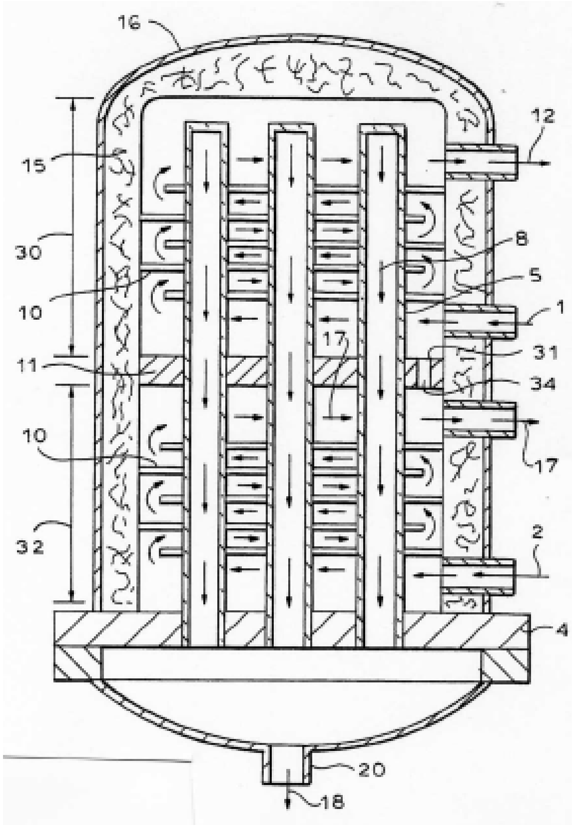


FIG 28

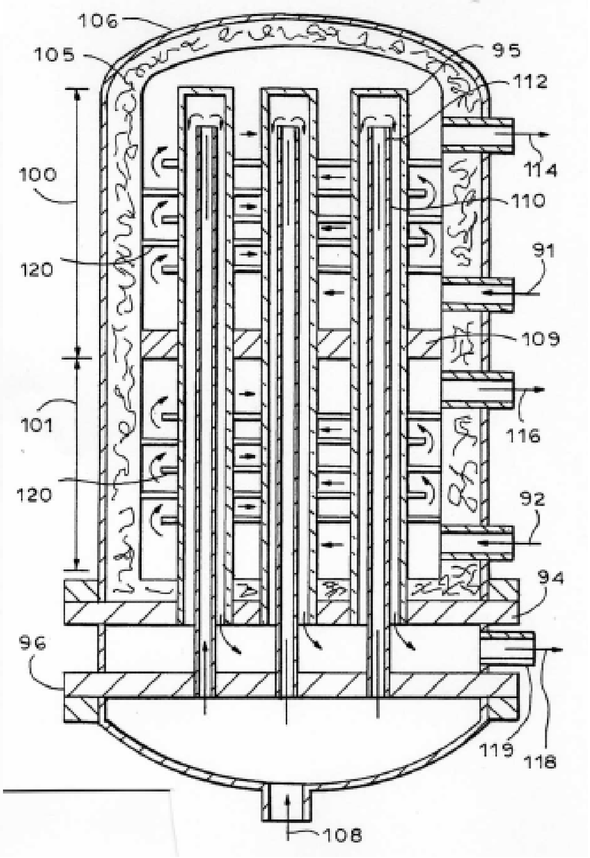


FIG 29

In Fig 28, the air flow would be divided into a cool minor portion entering the bottom heat exchanger shell side at nozzle 2 and cooling the tube sheet and the permeate oxygen in the tubes. The product oxygen is removed via nozzle 18. The heated air exits via nozzle 17 below the dividing baffle 11. This minor air stream can now be added to the major heated air stream which enters the oxygen ion transport section at nozzle 1. The oxygen permeates through the dense mixed conducting layer into the tube while the non-permeate stream leaves via nozzle 12. A purge stream to facilitate O_2 permeation can be introduced via an internal tube 112 as shown in FIG 29. This arrangement requires a double tube sheet, items 94 and 96.

Praxair report robust performance of their OTM tubes with over 20,000 hrs operation at atmospheric pressure with no failure and the ability to endure multiple chemical and thermal cycles. Their tests have covered both the oxygen partial pressure driven permeation in oxidising environment to produce either pure O_2 or O_2 in a purge gas stream or in a reducing environment with a fuel gas on the oxygen permeate side of the membrane.

Praxair is continuing with a development programme on OTM tubes aimed at increasing the oxygen flux by a factor of 2 to 5, continuing their process and systems analysis work and continuing OTM testing and manufacturing development. Their target is to construct a pilot plant by 2010.

4.8.2 The OTM Applied to Oxyfuel Processes

This application consists of a reactor designed to raise steam with an array of OTM tubes interspersed with steam tubes FIG. 30 (REF. 28).

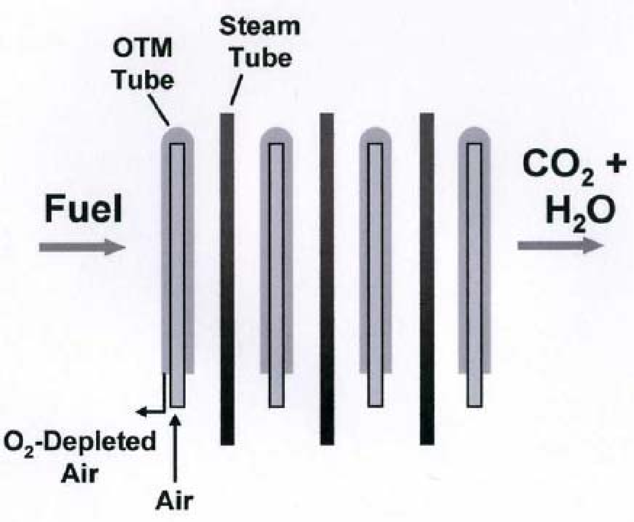


FIG 30

The air flow is within the tubes oxygen permeates to the shell side and a fuel gas circulates over the outside of the tubes. The heat released from the combustion which takes place is immediately absorbed by heat transfer into the adjacent steam raising tubes so that no excessive temperature rise will occur and no recycle is required. This concept is shown in FIG. 31 applied to a coal based gasification system supplied with O_2 from a cryogenic oxygen plant. The syngas is heated in a first OTM reactor with a controlled flux of oxygen to a temperature suitable for expansion of syngas to an intermediate pressure. The syngas then passes into the OTM boiler which raises high pressure steam for power production. The fully oxidised waste gas stream is cooled, water is separated, sulphur is removed as gypsum and the CO_2 product is dried, compressed and delivered to a pipeline. Praxair claims an overall efficiency for electric power production with CO_2 capture of 34.5% (LHV).

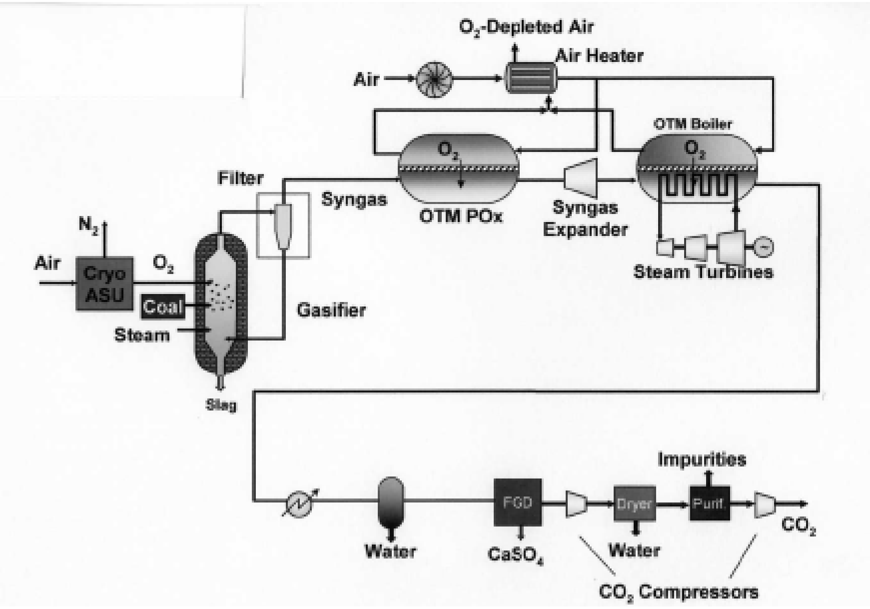


FIG 31

4.8.3 The OTM Applied to Gas Turbine Power Generation

The OTM applied to a pre-combustion decarbonisation of a natural gas fuel is shown in FIG. 32 (REF. 29)

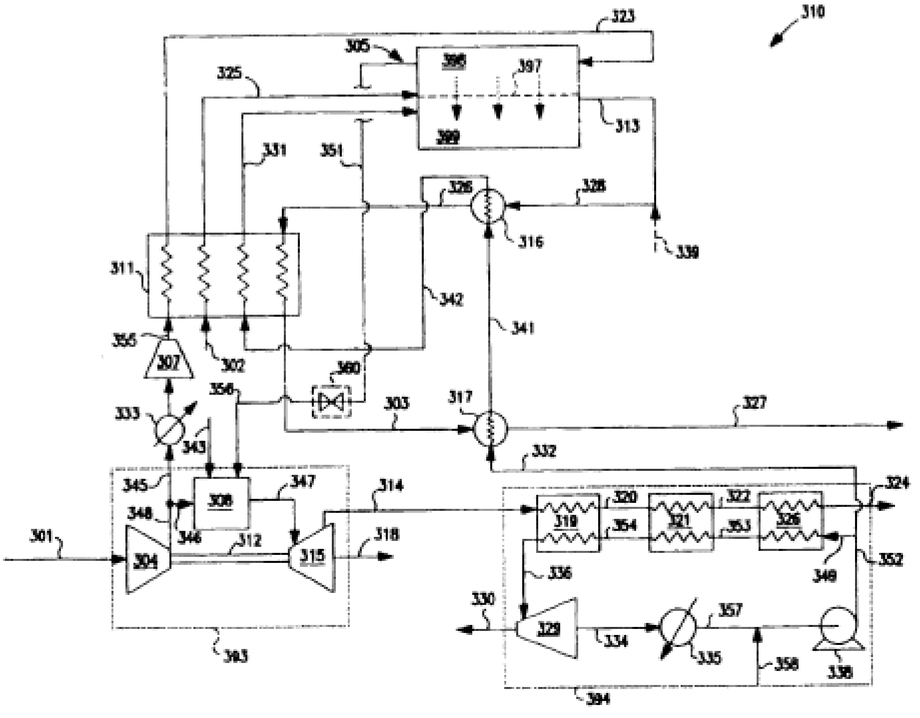


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FIG 32

A gas turbine 393, having a compressor section 304, supplies part of its air flow via a booster compressor 307 and heater 311 to the OTM unit 399 where O_2 permeates across the mixed oxygen ion conducting membrane 397. The Oxygen reacts with a fuel gas 325, such as natural gas and a moderator 331, such as water. Reactions occur as described in Section 4.3, resulting in the production of a synthesis gas mixture containing H_2 + CO which is cooled and delivered as a product gas 327. The exothermic reactions provide sufficient heat to maintain the desired operating temperature of the OTM unit. This gas can be converted to H_2 by shift conversion and CO_2 removal and used as a fuel gas in the gas turbine combustor 308. Alternatively part could be used to produce by-products such as H_2 for vehicle fuel or Fischer-Tropsch hydrocarbon liquids or methanol.

4.9 LINDE/BOC

4.9.1 The CAR Process

The Ceramic Auto-thermal Recovery Process (CAR) was originally proposed and investigated by the BOC Group (now part of the Linde Group). Unlike all the other processes for O_2 separation from air described, which use solid electrolyte, this process uses the mixed oxide perovskite materials at high temperature as oxygen adsorbents, taking advantage of the mobility of the oxygen ions in the crystal lattice at high temperature and the use of oxide materials which can be easily oxidised and reduced depending on the partial pressure of the gases in contact with the perovskite material. The mixed conductor functions as an oxygen acceptor at high oxygen partial pressures by providing the necessary electrons for oxygen ionisation from the metal ions which are thus raised to a higher valency state in the crystal lattice. A lower oxygen partial pressure reverses the process.

The CAR process uses two fixed beds of perovskite extrudates operating at higher temperature on a rapid 30 sec. cycle (REF. 30). Heated air passes upwards through one bed which removes O_2 while a flow of sweep gas having a low partial pressure of oxygen passes counter currently through the second bed to facilitate reduction and release of the oxygen from the perovskite material. It is possible to consider use of the recycled flue gas in an oxyfuel boiler system as the sweep gas. In order achieve oxygen concentrations of 25% to 30% required for an oxyfuel boiler operating with reasonable combustion temperatures on coal or liquid fuel it would be necessary to have a significantly higher pressure in the feed air than in the recycle flue gas. An additional problem with flue gas is the presence of ash, SO, SO_3, NO and NO_2 which may damage the adsorbent and the equipment. The preferred desorbing medium is a low pressure steam flow at about 1.6 bar pressure bled from an intermediate point in the low pressure steam turbine. The steam can be condensed from the steam/O_2 mixture and the low pressure O_2 is then available for the oxygen combustion process.

The high temperatures required for good oxygen transfer kinetics are retained in the bed by having a thick top and bottom layer of inert ceramic beads, which isolate the high temperature zone in the perovskite bed. The oxidation cycle is exothermic while the oxygen release cycle is endothermic. To maintain a heat balance on the system a small natural gas flow is introduced into the bed during the steam purge cycle which burns to CO_2 and water with the released oxygen. A CAR process integrated with an oxyfuel steam cycle power station is shown in FIG. 33 with a summary of the major parameters in TABLE 8.

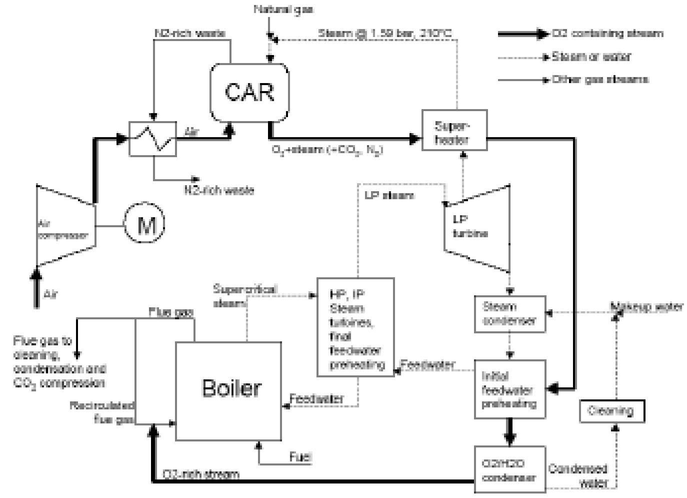
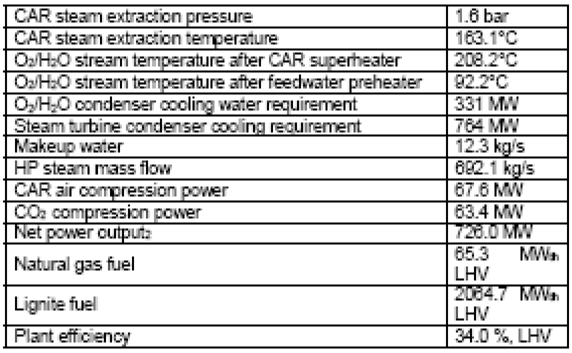


FIG 33



CAR steam extraction pressure	1.6 bar
CAR steam extraction temperature	163.1°C
O_2/H_2O stream temperature after CAR superheater	208.2°C
O_2/H_2O stream temperature after feedwater preheater	92.2°C
O_2/H_2O condenser cooling water requirement	331 MW
Steam turbine condenser cooling requirement	764 MW
Makeup water	12.3 kg/s
HP steam mass flow	692.1 kg/s
CAR air compression power	67.6 MW
CO_2 compression power	63.4 MW
Net power output$_2$	726.0 MW
Natural gas fuel	65.3 MW$_{th}$ LHV
Lignite fuel	2064.7 MW$_{th}$ LHV
Plant efficiency	34.0 %, LHV

TABLE 8

The base case boiler on which this study was based had an efficiency (LHV Basis) of 42.6%. This was reduced to 34% with the proposed CAR system. The developers claim a 27% reduction in power and a 50% reduction in capital cost compared to a cryogenic ASU. A 0.7 to 1.0 tonne O_2/day development unit has been built at the Western Research Institute in the US. The CAR process has been selected for further development by the European Union ENCAP CO_2 SP5 project.

4.10 Future development and implementation of O_2 ion membrane systems

The O_2 ion transport membrane technology is at present proceeding along parallel paths which are characterised by the geometry of the membranes which are being developed. The Air Products system uses hollow membrane wafers. The Norsk-Hydro system uses an extruded ceramic multi-channel combined heat exchanger and O_2 ion transport membrane unit. Praxair favours the use of tubular membrane geometry. The Linde Company uses a solid pelletised material in a partial O_2 pressure swing adsorption/desorption system. All these companies are using mixed oxide membrane compositions generally with perovskite crystal structure. The systems are configured either with an oxidising atmosphere or a fuel rich reducing atmosphere on the permeate side of the membrane. The technologies under development cover O_2 production for use particularly in IGCC or Oxy-fuel systems, the production of heat for power production with CO_2 capture, or the production of H_2 or (H_2+CO) gases. At this relatively early stage in the development of these highly diverse systems, it is difficult to predict the likely winners. Much will depend on the production cost of the complete membrane assembly integrated into the particular production unit. An important parameter is the surface area per unit volume of the membrane assembly which favours the Air Products and Norsk-Hydro configurations. The Air Products system seems to be at the most advanced stage of development. The application for IGCC O_2 production is planned to be demonstrated in the Futuregen project in the US, with start-up in 2012 and with an O_2 production requirement of about 2000 tonne/day. Full size membrane modules with a capacity of 0.5 tonne/day are currently under test and performance is reported to exceed design requirements. These wafers and fabricated modules are currently produced with a low volume production system which has been refined to develop optimum manufacturing procedures. The next stage of development will require a high capacity automated production line which must be capable of module production with consistently high and reproducible performance at minimum cost. The perovskite materials selected for the units appear to be capable of easily meeting their objectives for flux at required operating conditions. It will be necessary to confirm that performance can be maintained over a significant time span. There must be no undue change in the properties of the membrane caused either by changes in the internal composition or structure or caused by trace impurities in the feed air stream, such as dust. Norsk Hydro must demonstrate that they can operate their system reliably at the very high temperatures required for efficient operation, Praxair and The Linde Company all have similar problems in taking their technologies forward. Each company will need to reach a level of cost reliability and membrane life which will give their system a significant cost advantage over cryogenic O_2.

The key development objectives are as follows:

* Continuing refinement of the membrane and adsorbent materials to obtain high O_2 flux and stable composition particularly for the units operating with a reducing atmosphere on the permeate side which results in a huge difference in O_2 concentration leading to potential variation in composition and properties across the membrane.

* Long term testing of materials under operating conditions to verify life expectancy. Of particular importance is the ability to withstand temperature and pressure cycling and to achieve low failure rates.

* Optimisation of the membrane geometry and the complete membrane assembly to achieve the best hydrodynamic design, to meet performance objectives, to have a good mechanical environment for the membrane units giving low mechanical stress and vibration, and to integrate the assembly into the particular process system chosen.

* Development of the manufacturing process for the membrane elements to give reproducible high performance, low rejection rates and low cost.

* Demonstration projects at a reasonable scale to confirm performance targets, costs and reliability under real operating conditions.

The best indication of availability of large scale systems is the Futuregen operation which, if successful, would lead to O_2 units integrated with a gas turbine being marketed from perhaps 2014 onwards. For units operating under reducing conditions the present development targets are much less defined and no real dates can be given at his time.

5. REFERENCES

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6. GLOSSARY

ADIABATIC	Closed system with no heat transfer to the surroundings.
ADSORPTION	The uptake of molecules on the surface of a solid or liquid.
AIR INTEGRATION	Part or all of the air feed to an oxygen plant is provided from the compressor section of a gas turbine.
AMINE	An organic chemical compound containing one or more nitrogen atoms in groups -NH_2-, -NH or -N
ATR	Auto-thermal Reformer.
BITUMEN	A high density tar with a high carbon to hydrogen ratio.
CAR	Ceramic Auto-thermal Recovery process of the Linde Company (formerly developed by BOC Group)
CARBON DIOXIDE CAPTURE	The separation of CO_2 from a source.
CCS	Carbon Capture Storage.
CERAMIC	A non metallic dense coherent material capable of withstanding high temperatures.
CHEMICAL LOOPING	The separation of CO_2 in a fuel combustion process which has a circulating solid heat carrier which cycles between an oxidation stage using air and a reduction stage using fuel.
COLD BOX	An insulated container for cryogenic equipment.
COMBINED CYCLE SYSTEM	A power generation system with a gas turbine Brayton cycle coupled to a waste heat recovery unit generating steam for a Carnot cycle.
CO-PRODUCTS	Products other than power derived from hydrogen and carbon monoxide produced by gasification.
CRYOGENIC	A process operating generally at a temperature below -100^{o}C. (The upper temperature is not precisely defined).

ELECTROLYTE	A material which will conduct positive and negative ions in counter-current directions when a voltage difference exists.
ENDOTHERMIC REACTION	One that absorbs heat.
EQUILIBRIUM LINE	The equilibrium gas and liquid compositions for the more volatile component plotted on a McCabe Thiel diagram.
EXOTHERMIC REATION	One that releases heat.
FISHER-TROPSCH REACTION	The catalytic conversion of a 2:1 ratio H_2 to CO synthesis gas to high molecular weight hydrocarbons.
FLY ASH	Ash with a small particle size entrained in a gas flow.
GASIFICATION	A process by which a carbon containing fuel is reacted with air or oxygen and optionally water to produce a gaseous fuel which is predominantly carbon monoxide and hydrogen.
IGCC	Integrated Gasification Combined Cycle.
IEAG	International Energy Agency Greenhouse Gas R and D Programme.
INTERCOOLERS	Gas coolers placed between stages of a compressor.
ION	An atom or molecule that has acquired an electrical charge by gaining or losing an electron.
ISOTHERMAL	Constant temperature with heat transfer to the surroundings.
ITM	Ion Transport Membranes.
McCabe Thiel Diagram	A graphical picture of a distillation process which shows the gas and liquid compositions for a binary separation.
MCM	The Norsk-Hydro oxy-fuel combustion reactor plus heat exchangers.
MEMBRANE	A sheet or block of material which selectively separates the components of a fluid mixture.
NOX	Nitrogen oxides NO, NO_2 and N_2O.

OPERATING LINE	The lines which connect the composition of the more volatile component on each separation stage in a binary distillation plotted on a McCabe Thiel; diagram.
OXIDISING CONDITIONS	The loss of one or more electrons by an atom, molecule or ion.
OXYFUEL COMBUSTION	Combustion of a fuel with pure oxygen or a mixture of oxygen water and carbon dioxide.
OTM	Oxygen Transport Membrane.
PEROVSKITE	A hexagonal crystal lattice structure.
PERMEATE	The component which diffuses through a membrane.
PETCOKE	A carbon material derived from the oil refinery operation of coking.
PLATE FIN HEAT EXCHANGER	A heat exchanger having passages composed of finned sections held between parallel flat plates.
POLYMERIC	Fabricated from organic polymers.
POST COMBUSTION CAPTURE	The capture of carbon dioxide following processing after combustion.
POX	Partial Oxidation.
PRE COMBUSTION CAPTURE	The capture of carbon dioxide following processing of a fuel before combustion.
PRESSURE SWING ADSORBER (PSA)	A method of separating gases by using physical adsorption on a solid at high pressure and release at low pressure.
QUENCH	To cool a gas stream by direct water injection.
REDUCING CONDITIONS	The gain of one or more electrons by an atom, molecule or ion.
REBOILER CONDENSER	A heat exchanger in which one fluid is boiler while a second fluid is condensed.
SLAG	Molten ash.
STRUCTURAL PACKING	High specific surface area folded metallic sheet packing used in a mass transfer device such as a distillation column.

SUBCOOL	Cool a liquid below its boiling point.
SUPERCRITICAL	At a temperature and pressure above the critical point for the substance concerned.
SYNTHESIS GAS	A gas mixture containing as its major components carbon monoxide and hydrogen in proportions suitable for a chemical synthesis reaction.
WATER TUBE WALL	A system for containment of a hot gas from a burning fuel by tubes in which water is evaporated.