OXYGEN PRODUCTION TECHNOLOGIES FOR OXY

H. Katalambula

Dept. of Mechanical and Industrial Engineering,
College of Engineering and Technology,
University of Dar es Salaam.,
P.O. Box 35131 Dar Es Salaam Tanzania

ABSTRACT

Carbon dioxide, a dominating contributor to global warming is emitted to the atmosphere from power plants during combustion of coal. Oxy-fuel combustion is a new technology leading to a simplified sequestration of CO2. In this technology, fossil fuel is combusted with oxygen (instead of air) in such a way that the flue gas primarily consists of CO2, which can then be sequestered without significant processing. Part of the flue gas is used to dilute the oxygen in order to maintain the temperatures in the combustion process. The main energy penalty in oxy-fuel combustion is the cost of oxygen production. There are three major processes for air separation to produce oxygen, these are: cryogenic distillation, membrane separation and gas adsorption. Cryogenic distillation is well established process for large scale production but high energy consumption is the main disadvantage of this process. Membrane and adsorption processes are common for small and medium scale production. In gas adsorption, there are air separation techniques such as pressure and temperature swing methods. The production of oxygen with 90-95% purity and 5000+tpd production is the main challenge for this technology. At present the technology that can supply oxygen in large quantity is the cryogenic separation of oxygen from air. The papers aims at presenting a comprehensive review of the air separation technologies and identify areas that need attention so that oxy-firing can be achieved. The paper therefore looks at different technologies used for oxygen production, economic concepts as well as integration issues in the existing plants.

Key words: *oxy-fuel, oxy-firing, oxygen production, air separation.*

INTRODUCTION

Extensive use of fossil fuels has caused an increase in CO_2 emissions, resulting in a rapidly increasing atmospheric CO_2 concentration that in turn is cause global warming. Atmospheric CO_2 concentration needs to be stabilized at a low level if global warming is to be mitigated. The current estimated annual emissions of CO_2 world-wide from power generation using coal as fossil fuel has been reported to be over 9000 Mt/year (Energiläget, 2002).

There is a number ways through which reduction of greenhouse gases can be achieved. These include:
i) Improving efficiency in various combustion systems;
ii) Using alternate fuels which do not emit much greenhouse gases, such as biomass and nuclear power; and
iii) Implementing advanced technologies for CO_2 capture, such as:

a) Pre-combustion capture e.g. gasification;
b) Post combustion capture, such as the MEA adsorption; and
c) Oxy-fuel combustion

In conventional firing, air is fed for fuel combustion, and the major components in the flue gas include CO_2, N2, O2 and H_2O, with minor contents of SOx and NOx. Removal of SOx, NOx and particulate matter (PM) from the flue gas is usually required before its emission to the atmosphere in order to prevent environmental pollution. Separation and capture of CO_2 may be achieved by amine scrubbing (Energiläget 2002, IEA 2002), which is expensive. The capture of CO_2 would have been much easier if the flue gas was made up of only CO_2, a situation which can only be attained if pure O_2 is used for combustion. This technology is known as oxy-firing. Oxy-firing has recently attracted increasing research interests for its applications in coal, gas,

and oil combustion in many power plants (Wall et. al., 2004, Varagani et. al., 2004, Liljedahl et. al., 2001, Wilkinson et. al., 2001, Wilkinson et. al, 2003, Suratini et. al., 2009, McCauley et. al., 2009, Sturgeona et. al., 2009, Hjärtstam et. al., 2009, Okawa et. al., 1997, Smith and Klosek, 2001). The typical coal oxy-firing scheme is as shown in Figure 1 below:
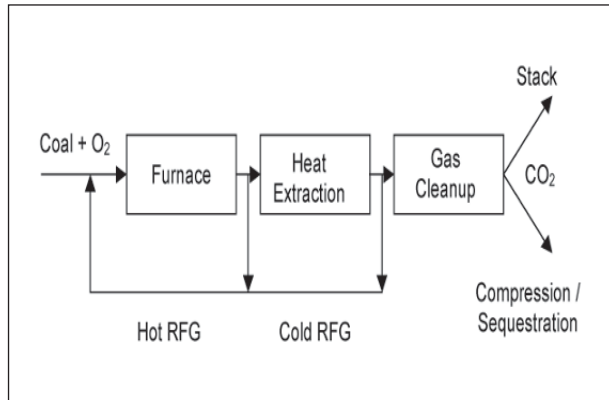

Fig. 1   Typical oxy-firing scheme for coal.

As can be seen from the figure, the oxy-firing involves the introduction of a fuel and a 95% pure O2 into the furnace. A major part of the flue gases formed (70-80%), which will be mostly CO2, is recycled back into the furnace in order to moderate the flame/combustion temperature. The recycled flue gas (RFG), can be hot, if recycled just after the furnace, or cold if recycled after some heat has been extracted from it. The remaining flue gas consists mainly of CO_2 and water vapor and small quantities of NOx and SOx. Compared to conventional air combustion, the flue gas treatment in oxy-firing process is much easier. Water can be separated simply by condensing the flue gas. Moreover, the absence of bulk nitrogen in the flue gas means that the equipment for flue-gas desulphurization and nitrogen/nitrogen oxide removal will have smaller volume, and thus be cheaper, than the corresponding equipment for air-fired power plants (Okawa et. al., 1997).

Despite all the merits of oxy-firing, the large scale production of O_2 still puts high penalty on efficiency and the costs are still high. This review therefore looks at different technologies used for oxygen production, economic concepts as well as integration issues in the existing plants.

TECHNOLOGIES FOR OXYGEN PRODUCTION

There are a number of technologies that are used in the O_2 production world-wide today, these include:
i)   Cryogenic,
ii)   Membrane separation and
iii)   Adsorption

Each of these has its advantages as well as disadvantages as far as production economics and product quality is concerned. Detailed account for each of the technologies is as given below:

Cryogenic technology

Cryogenic technology has contributed greatly to scientific research and has found wide range industrial applications. Cryogenic air separation technology has been successfully employed for many years to supply oxygen for the gasification of a wide range of hydrocarbon feedstock to generate synthesis gas for the production of fuels, chemicals and other valuable products (Smith and Klosek, 2001). An air separation unit (ASU) using a conventional, multi-column cryogenic distillation process produces oxygen from compressed air at high recoveries and purities. Cryogenic technology can also produce high-purity nitrogen as a useful byproduct stream at relatively low incremental cost. In addition, liquid argon, liquid oxygen, and liquid nitrogen can be added to the product slate for stored product backup or byproduct sales at low incremental capital and power costs (McCauley et. al., 2009).

Figure 2 illustrates the major unit operations required to cryogenically separate air into useful products. An air pretreatment section downstream of the air compression and after cooling removes process contaminants, including water, carbon dioxide, and hydrocarbons. The air is then cooled to cryogenic temperatures and distilled into oxygen, nitrogen and, optionally, argon streams. Various configurations of heat exchange and distillation equipment can separate air into the required product streams. These process alternatives are selected based on the purity and number of product streams required; trade-offs between capital costs and power consumption; and the degree of integration between the ASU and other facility units. Details on the cryogenic cycles are well presented by Smith and Klosek (2001) .
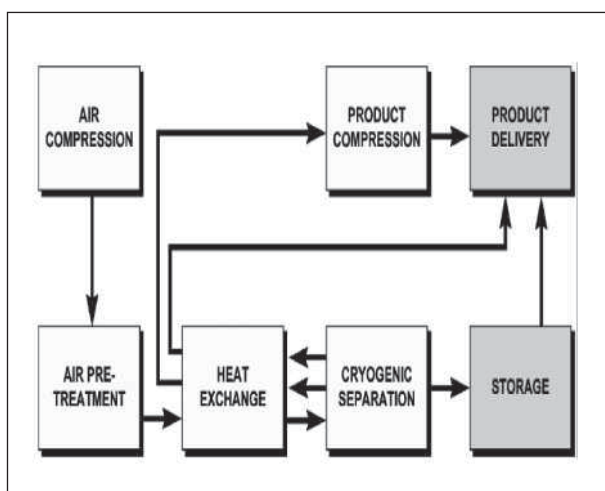
Figure 2: **Unit operations for a cryogenic air separation process: Source: Smith and Klosek, 2001.**

Oxy-firing using cryogenically supplied oxygen and flue gas recycle as a means of moderating combustion temperatures has been considered applicable for retro-fitting to process heaters and boilers at low technical risk, subject to a demonstration of the technology on a commercial scale. The cost of CO_2 capture utilizing this option is expected to lie in the range of \$35-40/ton (equivalent to an avoided cost in the range \$40-45/tonne). The overall scheme requires two world-scale cryogenic air separation plants (each providing 3,700 tones per day of 95 vol%, O_2), capturing 2 million tones per year of CO_2. The overall capture cost (\$/tone of CO_2 'avoided') for the basic scheme estimated by Air Products was found to be \$43/tonne, which compared favorably with benchmarked cost, generated by the CO_2 Capture Project (CCP) cost estimation team, of \$50/tonne. These costs included purification of the CO_2 [14]

Ion/Oxygen Transport Membranes for Air Separation

Membrane devices for gas or vapor separation usually operate under continuous steady-state conditions with three streams. The feed stream, a high-pressure gas mixture, passes along one side of the membrane. The molecules that permeate the membrane are swept using a gas on the other side of the membrane in the so-called permeate stream. The non permeating molecules that remain on the feed-stream side exit the membrane as the retentate stream. A pressure difference across the membrane drives the permeation process. Each gas component in a feed mixture has a characteristic permeation rate through the membrane. The rate is determined by the ability of the component to dissolve in and diffuse through the membrane material.

In order to improve the separation, new type membranes are required to have high permeability and selectivity, as well as long-term durability. Two areas of gas separation membrane research that are currently going on are polymer and inorganic membranes. Polymer membranes are relatively easy to manufacture and are suited for low temperature applications. The polymer morphology and mobility determine the gas permeability and selectivity. In addition, molecular sieve ability can be obtained by carbonizing polymeric materials. Inorganic membranes have much greater thermal and chemical stability. Appropriately sized pores in materials including zeolites and silica can act as molecular sieves that separate gas molecules by effective size. Surface adsorption and diffusion inside the pores can also play role in separating gas molecules (Boden et. al.

A typical membrane system is shown in Fig. 3. The main benefit of membrane separation is the simple, continuous nature of the process and operation at near ambient conditions. An air blower supplies enough head pressure to overcome pressure drop through the filters, membrane tubes and piping. Membrane materials are usually assembled into cylindrical modules that are manfolded together to provide the required production capacity. Oxygen permeates through a fiber (hollow fiber) type or through sheets (spiral wound) type and is withdrawn as product. A vacuum pump typically maintains the pressure difference across the membrane and delivers oxygen at the required pressure. Carbon dioxide and water usually appear in the oxygen enriched air product, since they are more permeable than oxygen for most membrane materials.

Membrane systems readily fit applications up to 20 tons/day, where air enrichment purities with water and carbon dioxide contaminants can be tolerated. This technology, as reported by Smith and Klosek (2001), is newer than adsorption and cryogenics and improvement in materials could make it attractive for larger oxygen requirements.
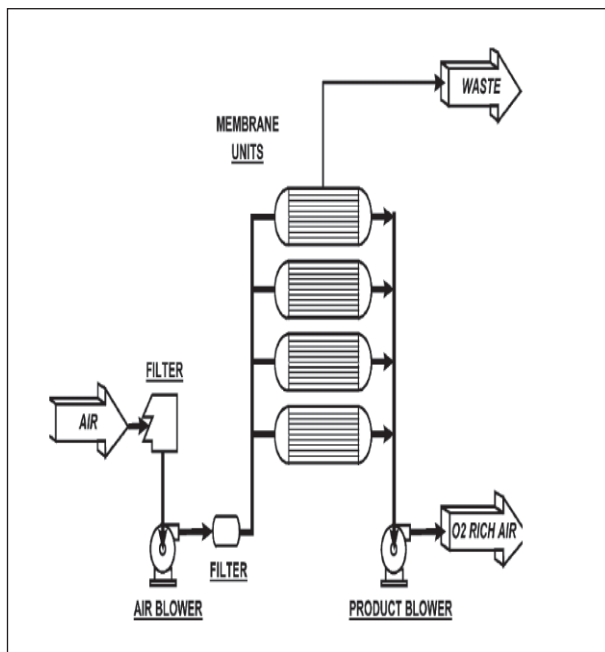
Figure 3:   Polymeric membrane air separation unit: Source Smith and Klosek. (2001)

Working on the same principle as membrane separation is another technology known as Ion Transport Membrane (ITM). ITMs are solid inorganic oxide ceramic materials that produce oxygen by the passage of oxygen ions through the ceramic crystal structure. These systems operate at high temperatures, generally over 600°C. Oxygen molecules are converted to oxygen ions at the surface of the membrane and transported through the membrane by an applied electric voltage or oxygen partial pressure difference, then re-form oxygen molecules after passing through the membrane material. Membrane materials can be fabricated into flat sheets or tubes.

For large energy conversion processes, the transport driving force is the pressure difference. Membranes, which operate by a pressure difference, are referred to as mixed conducting membranes since they conduct both oxygen ions and electrons. The oxygen ions travel through the ITM at very high flow rates and produce nearly pure oxygen on the permeate side of the membrane. The oxygen can be separated as a pure product, or another gas can be used to sweep on the permeate side of the membrane to produce a lower purity product.
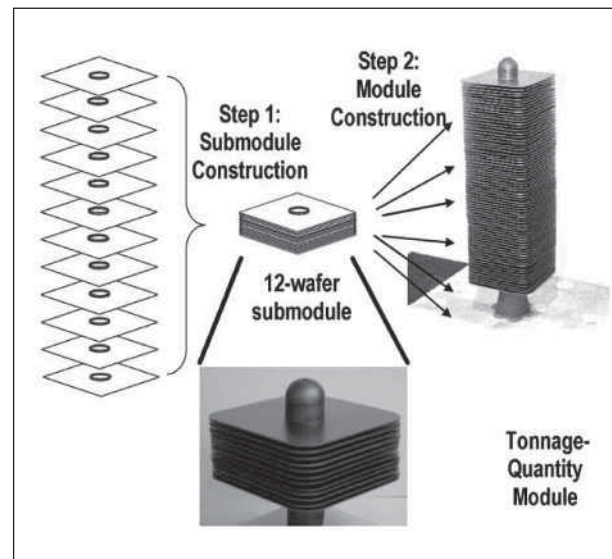

Figure 4:   Ion Transport Membrane System by Air Products Inc.

One company, Air Products and Chemicals Inc., is developing ion-transport membrane (ITM) oxygen separation technology for large-scale oxygen and advanced power production facilities including gasification. The development of ITMs will reduce the capital costs and parasitic load of air separation systems in comparison to the currently available cryogenic technology. Because air separation is a critical component of the gasification process for power production, any reductions in the cost of this component will in turn, reduce the overall costs of gasification, thereby making gasification more competitive. Figure 4 shows the construction of an ITM system.

Oxygen Permeation through the Hollow-Fiber

Despite the fact that polymeric membranes for gas separation are commercially available, they have so far not been an alternative for facilitated CO_2 capture in large-scale power production. Two important reasons for this are insufficient performance in terms of selectivity and flux, and secondly, they cannot be integrated very well into the power generation process due to a lack of high-temperature stability. Emerging polymeric membrane contactor systems, hybrid polymer membrane–solvent adsorption systems and new polymeric membranes could offer improvements, particularly for post-combustion capture in existing power plants. For the future, inherently more efficient power generation systems with integrated high-temperature separation

technology designed for CO_2 capture solutions, are highly desirable.

Gastight LaO.6SrO.4CoO.2FeO.8O$_3$ (LSCF) hollow-fiber membranes have been prepared by a phase inversion/sintering technique (Tan et. al., (2005). To obtain the dense hollow-fiber membranes, hollow-fiber precursors, spun from a starting solution containing LSCF powder, PESf binder, and PVP additive, must be heated at 1280°C for 4 hours

Apart from the pressure difference that has been mentioned above as the transport driving force in the membrane separation systems, temperature also plays a significant role. Tan et. al (2005)] reported the effect of temperature on oxygen permeation as shown in Figure 5, where both the downstream oxygen concentration and the permeation flux, represented by JO$_2$, are plotted for a constant sweep gas flow rate of 32.4 cm^3/min. As can be seen, the oxygen permeation flux increases noticeably with increasing the temperature, although the downstream oxygen partial pressure is also increased simultaneously. This means that the operating temperature plays a more important role in the oxygen permeation than the concentration driving force for the LSCF membranes
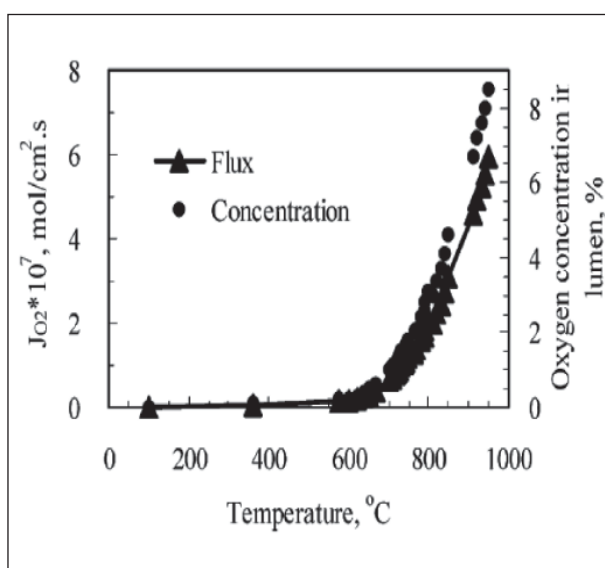

Figure 5: Effect of temperature on the oxygen permeation. Source: Ref. 15

In addition, Figure 5   indicates that the oxygen permeation flux in the LSCF membrane increases substantially after the temperature approaches 700 °C as a result of the order disorder transition of the oxygen vacancies reported by Tan et. al., (2005) As the flow rate of the sweep gas is increased, the oxygen partial pressure on the downstream side (lumen) would also change, resulting in different oxygen permeation fluxes. What is shown in Figure 6 is the experimental permeation data as a function of the downstream oxygen partial pressure at different temperatures for an oxygen partial pressure outside the membrane (upstream side) that was kept constant (atmospheric) through the continuous introduction of air. As expected, the oxygen permeation flux generally decreases as the downstream oxygen partial pressure is increased because the driving force for oxygen permeation is decreased. However, if the downstream oxygen partial pressure is very low, the value of the oxygen flux is dependent on the operating temperature and the oxygen permeation flux would slightly decrease even though the downstream oxygen partial pressure is decreased, especially at lower operating temperatures. The authors note that the oxygen permeation in the LSCF hollow-fiber membranes in this case follows a different mechanism and they call for further studies in the future. Figure 6 also indicates that the oxygen permeation flux increases with increasing temperature under the same oxygen partial pressure driving force. At the temperature of 900 °C for example, the oxygen permeation flux reaches 5.49×10^{-7} mol/(cm^2 s) for downstream oxygen partial pressure of 0.017 atm. This value is much higher than the oxygen permeation flux of 1.57×10^{-7} mol/(cm2s) through an LSCF tube membrane obtained at the same operating temperature and at the downstream oxygen partial pressure of 1×10^{-3} atm. Such an increase in the oxygen permeation flux obviously results from the improved membrane design, i.e., better membrane surface morphology and reduced membrane thickness.
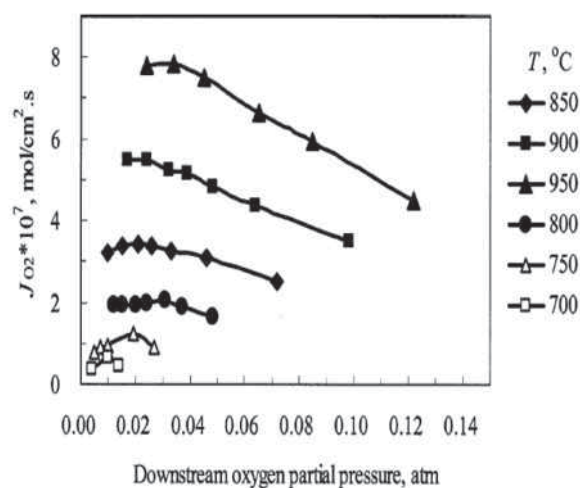
Figure 6: Plot of oxygen flux against downstream oxygen partial pressure at different temperatures. Source: Tan et. al. (2005)

Generally, what can be concluded from here is the fact that the operating temperature plays an important role in the oxygen permeation through the LSCF membranes than the concentration driving force. Additionally, once the operating temperature is above 700 °C, the oxygen permeation flux increases sharply as a result of an order-disorder transition of oxygen vacancies. The oxygen permeation flux through the LSCF hollow membrane is, in general, higher than that through LSCF disk-shaped or tubular membranes for the reasons mentioned above.

Adsorption Technology

For oxygen production, membrane separation is limited to a single-stage process for economic considerations; therefore, the purity of oxygen is limited to 50mol %. At larger throughputs and higher purities, the economic advantages shift to adsorption processes. With the introduction of pressure swing adsorption (PSA), adsorption processes have gained wide acceptance in industry for gas separation. Among the diversity of the adsorbents and process designs for air separation, two basic types of separations exist, namely equilibrium-controlled and kinetic-controlled separations (Tan et al. 2005).

Equilibrium-controlled separation is achieved by exploiting the difference in the adsorption isotherms or the adsorption capacities of the two major components, N_2 and O_2. In this case, both oxygen and nitrogen have rapid diffusion rates in the adsorbents, and separation depends on the preferential adsorption of nitrogen. For kinetic-controlled processes, separation is accomplished by taking advantage of the faster adsorption rate for oxygen than nitrogen because of the difference in molecular size. In kinetic-controlled processes, the choice of cycle time is critical for the performance of the adsorption process. In air separation, equilibrium controlled processes are used mainly for the production of oxygen, whereas the production of nitrogen is very often a kinetic-controlled process. The performance of adsorption system depends highly on the properties of adsorbents (Yang et. al., 2002). Generally, good adsorbents require:

- high selectivities,
- large adsorption capacities,
- fast sorption and desorption kinetics, and
- ease of regeneration.

For air separation, significant progress has been made in developing adsorbents with better sorption properties. In the production of oxygen, zeolite 5A and X have been extensively used. It has been reported that zeolites with low silicon/aluminum ratios are more selective for the adsorption of nitrogen. Nitrogen has a greater quadrupole than oxygen, thus the interaction between nitrogen and the cations in the zeolite is much stronger than that between oxygen and the cations. Moreover, the adsorption capacity of nitrogen is much more sensitive to the choice of cation present in the zeolite. With these considerations, extensive studies have been reported on the synthesis of ion-exchanged zeolites with different cations and improved properties. Coi et al. (1984), Sircar et al. (1985) and Chao et al. (1989) reported on Li-X zeolites with excellent N_2 adsorption capacities and selectivities. Ca- and/or Sr-exchanged lithium-X zeolites exhibit good sorption properties for nitrogen (Baksh et. al.). Binary Li- and Ag-exchanged zeolite X sorbents showing good nitrogen to oxygen selectivity as reported by Coe et. al. (1992) and large working capacities were also reported by other researchers such as Rege et. al. (1997) and Hutson et. al. (1999).

Despite the progress made on both process design and adsorbent development, current industrial adsorption processes for air separation still suffer

from the following drawbacks:

a)   The selectivity of nitrogen to oxygen on zeolite sorbents is still not high enough for efficient separation. At present, the highest thermodynamic selectivity achieved is around 10.

b)   Adsorption properties often deteriorate dramatically in the presence of other components, especially water and carbon dioxide. Pretreatment is definitely required to maintain the performance of the major adsorbents in the system, which makes process design more complicated.

c)   For most zeolite sorbents, there is no thermodynamic selectivity of adsorption between oxygen and argon under normal conditions because of their weak or nonpolar nature and comparable polarizabilities.

By using equilibrium-controlled adsorption processes not in combination with other processes, the highest purity of oxygen achieved is about 95-96%, which is not suitable for some applications. Furthermore, it would be highly desirable to develop an adsorption process in which the adsorbed component is oxygen with very high purity. New and more efficient sorption process can therefore be developed only when new sorbents are discovered. Lin et al. (2000) disclosed in a U.S. patent a new group of sorbents for air separation and oxygen removal for which all of the above drawbacks had possibly been eliminated. These sorbents are oxygen-deficient perovskite-type ceramics that can selectively adsorb considerable amount of oxygen at high temperatures (>300 °C). This group of the sorbents theoretically has an infinitely high selectivity for oxygen over nitrogen or other non-oxygen species. The effects of the presence of other gases on the separation properties of these new sorbents are expected to be minimum. Unlike all previously reviewed sorbents, these perovskite-type ceramic sorbents should be operated at high temperatures because of the inherent thermodynamics and kinetics involved in the oxygen sorption process.

High-temperature separation of oxygen has recently received increasing interest from industrial gas companies. Thus, in air separation, nitrogen molecules are more strongly adsorbed than oxygen or argon molecules. As air is passed through a bed of zeolitic material, nitrogen is retained and an oxygen-rich stream exits the bed. Carbon molecular sieves have pore sizes on the same order of magnitude as the size of air molecules. Since oxygen molecules are slightly smaller than nitrogen molecules, they diffuse more quickly into the cavities of the adsorbent. Thus, carbon molecular sieves are selective for oxygen and zeolites are selective for nitrogen.
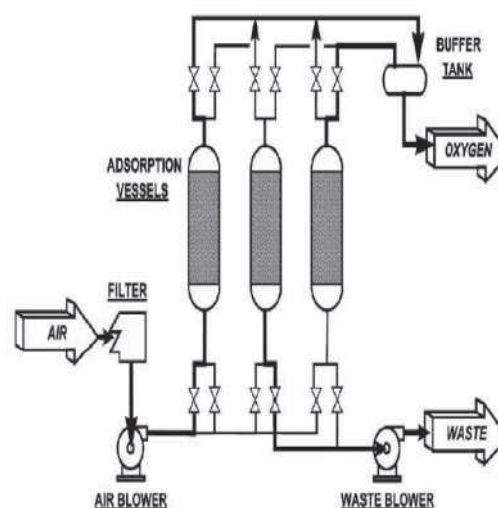

Figure 7:   Adsorption-based   air   separation process

Zeolites are typically used in adsorption-based processes for oxygen production and a typical flow sheet for this is shown in Fig. 7. Pressurized air enters a vessel containing the adsorbent. Nitrogen is adsorbed and an oxygen-rich effluent stream is produced until the bed has been saturated with nitrogen. At this point, the feed air is switched to a fresh vessel and regeneration of the first bed can begin. Regeneration can be accomplished by heating the bed or by reducing the pressure in the bed, which reduces the equilibrium nitrogen holding capacity of the adsorbent. Heat addition is commonly referred to as temperature swing adsorption (TSA) and pressure reduction as pressure or vacuum swing adsorption (PSA or VSA). The faster cycle time and simplified operation associated with pressure reduction usually makes it the process of choice for air separation.

Yang and Lin (2005) reported that another important application of a perovskite ceramic sorbent-based production of an O_2-enriched CO_2 stream could be envisioned if CO_2 is used to replace O_2 from the

sorbent column, and it was first illustrated in their recent publication. Under this system, during the O_2-adsorption process, air is used as feed gas to saturate the perovskite-type ceramic sorbent with O_2; while during the O_2-desorption process; CO_2 is swept through the column to desorb O_2 from the sorbent to produce an O_2-enriched CO_2 gas. From the preliminary fixed-bed studies reported by Yang and Lin (2005), this sorption process can efficiently separate oxygen at high temperature and allows productions of O_2 enriched CO_2 stream with an average oxygen concentration around 45% and a maximum oxygen concentration up to 80%, which could be directly fed into the boiler for fuel combustion. Furthermore, the high temperatures during sorption processes can be easily maintained due to the hot CO_2 gas, which can be obtained from flue gas and the energy consumption can thus be reduced. This process is a promising alternative to the conventional cryogenic air separation for production of oxygen enriched streams. A fundamental study on this sorption process indicates that production of oxygen-enriched carbon dioxide stream is based on the following reversible reaction as proposed by Yang and Lin (2005):

Lao.1Sro.9Co0.5Feo.502.6 $+0.9CO_2$ $\Leftrightarrow$ $0.9SrCO_3$ $+o.o5La2O_3 +0.5CoO +0.25Fe2O_3 +0.15O_2$ (A)
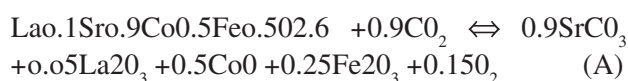
The kinetics of reaction A and its reverse reaction both exhibit high reaction rate in the initial stage followed by a low rate in the second stage. Efficiency of the sorption process should depend on operation conditions. This work specifically aimed at studying the effects of operation conditions including the flow rate of feed gas during sorption and desorption steps, adsorption time, and the operation temperatures on

both oxygen adsorption and desorption processes. Four parameters, i.e., oxygen concentration, the oxygen recovery, carbon dioxide recovery and productivity, were defined to evaluate the efficiency of the separation process.

Table 2 shows the separation parameters at different adsorption temperatures. The oxygen recovery, CO_2 recovery, average oxygen concentration in the desorption effluent, and productivity increases with increasing adsorption temperature. This is because of larger amount of oxygen adsorbed due to faster sorption kinetic at a higher adsorption temperature (for fixed adsorption time). The four separation parameters for adsorption at 850 ÐC are very close to those at 900 ÐC. If the energy cost in oxygen separation is considered, 850 ÐC might be the optimal adsorption temperature. The separation parameters with desorption step at 800 and 900 ÐC are summarized in Table 3.

As seen in Table 3, the average oxygen concentration, oxygen recovery, CO_2 recovery and productivity are all improved with increasing desorption temperature. The more efficient desorption process at the higher desorption temperature is due to the faster kinetics of reaction A. Moreover, at higher temperatures, the perovskite-type sorbent may also undergo the following defect reaction in the initial stage of exposure to CO_2

Oo× +2h• = (1/2) O_2 (g) + Vo•• (D)
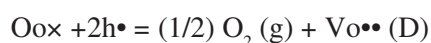
Where Oo× is the lattice oxygen, Vo•• the oxygen vacancy and h• is the electronic-hole. Thus, extra oxygen is generated during the desorption step at high temperatures.

Table 2: Effect of adsorption temperature on the separation process

Adsorption temperature (C)	Time range to collect the product in desorption (s)	Average Oxygen concentration (%)	Air recovery (%)	CO_2 recovery (%)	Productivity (ml/min)
800	420-603	39.6	6.62	11.4	0.113
850	95-805	48.6	8.18	12.8	0.132
900	568-906	48.9	9.80	12.9	0.157

Table 3:   Effect of desorption temperature on the separation process

Adsorption temperature (C)	Desorption temperature (C)	Time range to collect product in desorption (s)	Average oxygen concentration (%)	Air recovery (%)	CO_2 recovery (%)	Productivity (ml/min)
800	800	420-603	39.6	6.62	11.4	0.113
800	900	210-510	50.1	15.3	34.0	0.260
850	900	220-670	58.8	18.7	26.6	0.272

A substantial amount of work was done to investigate reversibility of the sorption process where five cycles of adsorption and desorption were continuously monitored. Results showed a good reversibility of the sorption and desorption processes. However, morphology of sorbent appeared to be somehow changed to a more dense structure after cycles of sorption process, which might vary the packing efficiency of sorbents and affect the reversibility in the even long-term operation.

In a separate study by Misuzaki et al. (1984), the adsorption and desorption of oxygen using the perovskite-type ceramic LSCF as sorbent were studied by the fixed-bed experiments. Effects of operating conditions, including adsorption time, flow rates of adsorption and desorption feed gases, and adsorption and desorption temperatures, on separation efficiency were investigated in terms of oxygen concentration of the product stream, oxygen recovery, carbon dioxide recovery and productivity. Experimental results showed that a shorter adsorption time gives lower desorption efficiency but higher productivity, hence a proper adsorption time exists for the best performance. Increasing the air feed flow rate in a certain range (<10 ml/min) during adsorption can improve the oxygen concentration in the product stream and CO_2 recovery at the expense of oxygen recovery.

Increasing CO_2 feed flow rate during desorption within 10 ml/min could enhance the reaction kinetics in the initial desorption stage, resulting in an increase of the average oxygen concentration in the effluent. However, it decreases the oxygen recovery due to the shorter desorption duration, and increases CO_2 recovery due to slower CO_2 reaction rate in the second stage as compared to the CO_2

feed rate. Furthermore, increasing either adsorption temperature or desorption temperature helps improve greatly the oxygen concentration, oxygen recovery, CO_2 recovery and productivity. It has been found that 850 and 900ÐC are the optimal adsorption and desorption temperatures. Combination of the two optimal temperatures in the adsorption and desorption processes makes a remarkable improvement for oxygen separation, with average oxygen concentration, oxygen recovery, carbon dioxide recovery and productivity, respectively, of 58.8%, 18.7%, 26.6% and 0.272 ml/min (Misuzaki et. al., 1984) .

PERTINENT ISSUES

Comparison of the Different Oxygen Production Methods.

A review by Smith and Klosek (2001) gave a detailed comparison between the different techniques currently being used in O_2 production. It is apparent from the review and the current trend that adsorption and polymeric membrane processes will continue to improve in both cost and energy efficiency since there is a lot of ongoing research and development activities on both adsorbents and membrane materials. However, neither of the technologies is expected to challenge cryogenics for large tonnage and purity, in the near future. Another side effect of chemical processes is the material corrosion problems and this can affect technology development on these processes. On the other hand, Ion Transport Membrane technology is seen as the best candidate to challenge cryogenics for the production of high purity, large quantity O_2.

Table 4: Comparison of O_2 production technologies

Process	Status	Economic range (sTPD)	Byproduct capability	Purity limit (vol.%)	Start-up time
Adsorption	semi-mature	<150	poor	95	minutes
Cryogenic	mature	>20	excellent	99	hours
Membrane	semi-mature	<20	poor	~40	minutes
ITM	developing	undetermined	poor	99	hours

Smith and Klosek (2001) presented a comparison of different O_2 production technologies and their summary is as shown in Table 4. The criteria for comparison are defined as follows: Economic Range is the typical production range where the technology is currently economically feasible. The less efficient, but less complex adsorption and polymeric membrane systems are favored at the lower production rates. Byproduct capability is a measure of the ability of the process to produce relatively pure nitrogen or argon streams without add-on deoxo or cryogenic systems. Purity limit is the maximum purity that can be economically produced using the specific technology. All the technologies are capable of producing lower purities than the maximum by adjusting process conditions or by blending purer oxygen product with air. Start-up time is a measure of the time required to restart the process and reach a given purity after a shutdown.

Integration

Introduction of air separation units (ASU) in any industrial set-up will require ensuring that it can be successfully integrated into the whole system. The integration should aim at making the whole set-up more economical as well as technically feasible. This should look at issues such as the utilization of by-products, recovery of heat for re-use into the system, etc. Proven integration concepts include the use of air extracted from the gas turbine's compressor to feed the ASU. Smith and Klosek (2001) have given a number of integration concepts, whereby in one of the configurations, byproduct nitrogen from an ASU can be compressed, heated against extraction air, and injected in a gas turbine's combustor. Generally, ITM Oxygen integrates well with turbine based power cycles. Successful embodiment of ITM Oxygen with

advanced power cycles will:

- increase efficiencies and environmental performance
- reduce the capital and operating costs of coal-based energy plants.

Additionally, the use of CO_2 as sweep gas makes the integration of adsorption technology into combustion system easier (make use of flue gas)

CONCLUSION

From the current study, it is quite clear that oxy-firing is an attractive process for a number of reasons as presented above. However, the quantity of O_2 required and its purity necessitates the development of newer technologies to produce O_2 of the required quality. Apart from cryogenic process, other technologies are still under development and will take time to mature. There are also a number of promising avenues, such as the use of LSCF as adsorbent which will be capable of producing O_2 at higher purity and larger quantities.

REFERENCES

Baksh, M. S. A, Kikkinides, E. S,and Yang, R. T., (2000) Lithium Type-X Zeolite as a Superior Sorbent for Air Separation. Sep. Science Journal.

Boden,J.Miracca,I.,Aasen,K.I.,"OxyfuelOverview, CO_2 Capture Project Report

Chao, C. G,and Millwood, N. Y., (1989) Process for separating nitrogen from mixtures thereof with less polar substances. U.S. Patent 4, 859, 217.

Coe, C. G., Kirner, J. F., Pierantozzi, R.and White, T. R., (1992) Nitrogen adsorption with a Ca and Sr exchanged lithium Z zeolite.U.S. Patent 5,152,813, 1992.Technol. 27 (23), 277.

Coi, C. C. and Steven, M. (1984) Polyvalent ion exchanged adsorbent for air separation. U.S. Patent 4, 481, 018.

Energiläget (2002) (The Energy Situation), Swedish National Energy Administration, Publication ET 18:2002.

Hjärtstam, Stefan, Klas Andersson, Filip Johnsson, Bo Leckner, (2009) Combustion characteristics of lignite-fired oxy-fuel flames, Fuel 88, 2216–2224.

Hutson, N. D., Rege, S. U. and Yang, R. T. (1999) Mixed Cation Zeolites: LixAgy-X as a Superior Adsorbent for Air Separation. AIChE J., 45 (4), 724.

IEA World Energy Outlook (2000).

Liljedahl, G, Marion, J, Nsakala, N.Y, Bozzuto, C, Palkes, M, Vogel, D, Gupta, J.C, Guha, M, Johnson, H, and Plasynski, S., (2001) Technical and economic Feasibility of CO2 capture on an existing US coal-fired power plant, in Proceedings of the 2001 International Joint Power Generation Conference, New Orleans, LA, USA.

Lin, Y. S., McLean, D. L. and Zeng, Y., (1983) High-Temperature Adsorption Process. U.S. Patent 6,059,858, 2000. DC, Vol. 235, pp 71-86.

McCauley, K.J, Farzan, H, Alexander, K. C, McDonald, D.K, Varagani, R, Prabhakar, R, Tranier, J-P, and Perrin, N., (2009) Commercialization Of Oxy-Coal Combustion: Applying Results Of A Large 30mwth Pilot Project, GHGT-9, Energy Procedia 439-446.

Mizusaki, J, Yamauchi, S., Fueki, K, and Ishikawa, A., (1984) Nonstoichiometry of Perovskite-type oxides La1–xSrxCoO3–δ, Solid State Ionics 12,119.

Okawa, M, Kimura, N, Kiga, T, Takano, S, Arai, K and Kato, M, (1997) Trial Design for a CO2 recovery plant by burning pulverized coal in O2/CO2, Energy Convers. Manage. 38 (Supply.) 123–127.

Rege, S. U and Yang, R. T., (1997), Limit for Air Separation by Adsorption with LiX Zeolite. Ind. Eng. Chem. Res. 36 (12), 5358.

Sircar, S.; Conrad, R. R.and Ambs, W. J., (1985) Binary ion exchanged type X zeolite adsorbent. U.S. Patent 4, 557, 736.

Smith A and Klosek J, (2001) A review of air separation technologies and their integration with energy conversion processes Fuel Processing Technology 70.115–134.

Sturgeona, D.W, Camerona, E.D, Fitzgeralda, F.D, (2009) Demonstration of an oxyfuel combustion system, GHGT-9, Energy Procedia 471-478.

Suraniti, Silvestre L., Nsakala ya Nsakala , and Scott L. Darling, (2009) Alstom Oxyfuel CFB boilers: a promising option for CO2 capture, GHGT-9, Energy Procedia 543–548.

Tan Xiaoyao, Liu Yutie, Li K, (2005) Preparation of LSCF Ceramic Hollow-Fiber Membranes for Oxygen production by a Phase-Inversion/Sintering Technique, Ind. Eng. Chem. Res. 44, 61-66.

Varagani, R, Chatel-P´elage, F, Pranda, P, Lu, Y, Chen, D Rostam-Abadi, M, Farzan, H, Vecci, S.J, and Bose, A.C, (2004) Oxycombustion in pulverized Coal-fired boiler: a promising technology for CO2 capture, in: Proceedings of Third Annual Conference on Carbon Sequestration, Alexandria, VA, USA.

Wall, T, Sheng, C and Gupta, R., (2004) Oxy-fuel combustion for sequestration Ready CO_2-technology status, assessment and research needs, in: Proceedings of the 14th IFRF

Wilkinson, M.B, Boden, J.C, Panesar, R.S, and Allam, R.J., (2001). CO_2 capture via Oxyfuel firing: optimization of a retrofit design concept for a refinery power station boiler, in: Proceedings of First National Conference on Carbon Sequestration, Washington, DC, USA.

Wilkinson, M.B, Simmonds, M, Allam, R.J, and White, V., (2003) Oxyfuel conversion of heaters and boilers for CO_2 capture, in: Proceedings of Second National Conference on Carbon Sequestration, Washington, DC, USA.

Yang, Q, and Lin, J.S.Y., (2005) Perovskite type ceramic sorbets for production of oxygen enriched carbon dioxide stream, AIChE J. 2005.

Yang Zhaohui, Lin Y S, and Zeng Y, (2002) High-Temperature Sorpton Process for Air Separation and Oxygen Removal, Ind. Eng. Chem. Res. 41 (11), 2775-2784