

Hybrid membrane/cryogenic separation of oxygen from air for use in the oxy-fuel process

Thomas Burdyny, Henning Struchtrup*

Department of Mechanical Engineering, University of Victoria, P.O. Box 3055, Victoria BC, V8W 2Y2 Canada

ARTICLE INFO

Article history:

Received 1 May 2009

Received in revised form

12 November 2009

Accepted 22 December 2009

Available online 1 March 2010

Keywords:

Air separation

O₂/N₂ permeable membranes

Cryogenic distillation

Oxy-fuel process

ABSTRACT

The process of oxy-fuel combustion requires the separation of oxygen from air on a large scale for use in the combustion chamber. This separation is currently done through energy intensive cryogenic distillation. To reduce the overall energy requirements for air separation it is examined whether a hybrid membrane and cryogenic process be utilized instead. The examined process uses an O₂/N₂ permeable membrane to create oxygen enriched air. This enriched air is then turned into high purity oxygen using cryogenic distillation. Several arrangements of such a system are investigated and compared on a practical and thermodynamic level to the current cryogenic process in use. It is found that using a vacuum pump arrangement to draw air through the membrane has potential to reduce energy requirements from the current standard. It is also found that the hybrid system is more productive in small to medium scale applications than in large scale applications because of the increased irreversibilities in the cryogenic process at smaller scales.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Oxygen production from air separation is used in many applications worldwide such as medical devices, steel and chemical manufacturing, and most recently carbon capture on a large scale. Historically, the size of the operation and the required purity of oxygen determine the method of separation [1].

Presently, a widely discussed process for carbon capture is the oxy-fuel process, in which the oxidizer for the power plant is pure oxygen mixed with power plant exhaust [2]. Thus, the final exhaust is essentially only carbon dioxide and water, which can be easily separated; the carbon dioxide is then stored in underground caverns, e.g., depleted oil or gas fields. The process of oxy-fuel combustion requires high purity oxygen in large quantities. For oxy-fuel processes such as the combined cycle, Graz cycle [3] and Water cycle [4] the oxygen separation process, however, would be an addition to an existing power plant and the work required to separate oxygen from air becomes an energy penalty for the power plant to operate with sequestration [5]. Oxy-fuel cycles which require no additional energy for air separation such as Chemical Looping Combustion [6] are also proposed but still require significant development. Kvamsdal et al. [7] show that a gas turbine combined cycle power plant installed with the oxy-fuel process will reduce the overall plant

efficiency from 56.7% to 47%. Approximately 8.8% of the efficiency loss comes from the work required to produce and compress oxygen for combustion through cryogenic distillation in the Linde process. Thus, if the separation process can be improved by even a small margin, the oxy-fuel process will benefit substantially.

The three branches of technologies that currently exist to separate oxygen from the air include distillation, adsorption and membranes [8]. Distillation is the most mature of the three technologies and allows for both high purities (>99%) and large scale productions [9]. Adsorption is able to reach purities of up to 95% oxygen but the requirement of solvents limits its size capacity due primarily to capital costs [1]. Membrane technology is the most recent of the three and includes polymeric and high temperature ion transport membranes. While polymeric membranes can produce oxygen enriched air of various concentrations, ion transport membranes can produce purities of close to 100%. Both membranes however have yet to be built for large scale gas separations [1]. A combination of the above technologies for the production of high purity oxygen has been suggested [10] but no detailed research has been completed discussing either energy costs or integration to the oxy-fuel cycle. Several papers though have discussed the possibility of combining these technologies for various other purposes such as the production of argon [11] and the recovery of CO₂ [12].

The hypothesized design to create pure oxygen using less energy utilizes both membrane and cryogenic technologies. With an induced pressure difference, an O₂/N₂ selective polymeric membrane can partly separate oxygen from air by having properties that allow

* Corresponding author. Tel.: +1 250 721 8916; fax: +1 250 721 6051.

E-mail addresses: tburdyny@uvic.ca (T. Burdyny), struchtr@uvic.ca (H. Struchtrup).

oxygen molecules to pass through the membrane easier than nitrogen molecules. However, the membrane cannot fully separate oxygen from the air; it can only be used to increase the concentration of oxygen as some nitrogen molecules will also flow through the membrane. The enriched air can then be processed in a cryogenic stage; this will require less work than if ambient air is used, since a smaller volume of gas needs to be processed in the cryogenic process to obtain the same amount of product, i.e. pure oxygen. Enrichment of the air using a membrane, however, introduces extra work irreversibilities in the form of additional compressors, turbines and blowers, and irreversibilities for the membrane flow. Depending upon the actual value of the various irreversibilities, using a combined membrane and cryogenic process may provide a smaller energy penalty than the cryogenic process alone; in the following, several arrangements are considered to test this hypothesis.

A compressor on the feed side of the membrane coupled with a recovery turbine for the waste gas can be used to create the required membrane pressure difference. Alternatively, a vacuum pump on the permeate side of the membrane can be used to create the pressure difference. Both configurations are thermodynamically modeled to determine the best method of air separation. The primary parameter in the system is the membrane selectivity which is a property of the membrane. The selectivity is varied to study the effect it has on the separation work. The effects of adding heat to the turbine inlet and varying the efficiencies of the compressor and turbine are examined as well. For large oxygen production rates (thousands of tons O₂/day) only the vacuum pump arrangements show improvement over the existing (i.e., cryogenic alone) design, while both variants of the hybrid design show improvements in small to medium scale productions (hundreds of tons O₂/day).

The remainder of this paper is organized as follows: Section 2 discusses the basic processes in membranes and cryogenic processes for air separation. In particular a detailed discussion of membrane separation is presented. In Section 3, various configurations for hybrid systems are introduced, including a discussion of the methodology behind the processes. The numerical results for the separation work of the various arrangements are graphed and discussed in Section 4 for both large and small scale productions rates, including the resulting effect on the oxy-fuel process. In the last Section, the effect of varying certain parameters is investigated and recommendations regarding the future of the hybrid system are discussed. Integration of the hybrid system to the oxy-fuel process and comparisons to ceramic membrane separation are also included in the discussion.

2. Current technologies for air separation

2.1. Membranes

The use of selective membranes for partial air separation progressed rapidly in the 1980s as a promising alternative to cryogenics and adsorption [13]. These membranes allow the passage of certain molecules easier than other molecules. For an O₂/N₂ permeable membrane, both oxygen and nitrogen can permeate through the membrane, but oxygen does so with more ease. Fig. 1

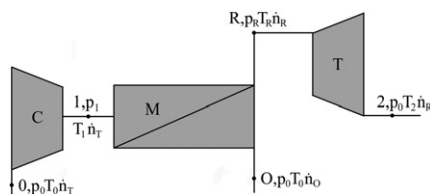


Fig. 1. Simple Membrane Process with a Compressor coupled with a Recovery Turbine.

shows the set-up of the basic process. To induce a flow of molecules across the membrane, a pressure difference must exist, which is created by a compressor. A recovery turbine is then placed downstream, so that the portion of the gas that did not pass through the membrane can be expanded and some of the compression work can be recovered. The oxygen enriched gas that did pass through the membrane is assumed to be at atmospheric pressure.

An alternative set-up to create the pressure difference is a vacuum pump on the permeate side as seen in Fig. 2. This configuration requires a blower to keep fresh, undepleted air flowing past the membrane. Otherwise oxygen depleted air would pool along the membrane reducing the amount of oxygen that passes through.

In the following, the subscript *R* indicates the nitrogen rich waste gas while the subscript *O* indicates the oxygen rich product gas. All gases are assumed to be ideal gases with constant specific heats.

Membrane permeability is different for each type of molecule and determines its ability to flow through the membrane. For a component γ , the mole flow through the membrane is given by

$$\frac{dn_\gamma}{dt} = Q_\gamma (p_{\gamma,0} - p_{\gamma,1}) \quad (1)$$

where Q_γ is the permeability of the membrane for a given component, and $p_{\gamma,0}$ and $p_{\gamma,1}$ are the partial pressures of the component before and after the membrane, respectively.

Technical membrane separation processes are continuous processes, where the source gas flows along the membrane while some of it penetrates to the other side. For the computation it is convenient to follow an initial amount n_T of source gas as it travels along the membrane and its components traverse the membrane. Then Q_γ is a parameter that depends on the initial amount considered and on the size of the membrane.

In an O₂/N₂ permeable membrane the ratio of the membrane permeabilities of oxygen and nitrogen, Q_{O_2} and Q_{N_2} , is the membrane selectivity, α , which is independent of the size of the system considered,

$$\alpha = \frac{Q_{O_2}}{Q_{N_2}} \quad (2)$$

The selectivity is dependent upon the type of membrane, the membrane material and the membrane configuration.

In order to gain independence of the system size, it is convenient to introduce a dimensionless permeation time scale as

$$\tau = tp_0 Q_{N_2} / n_T \quad (3)$$

The dimensionless permeation time τ measures the time that the gas is allowed to permeate through the membrane; it can be controlled by choosing the flow rate of the gas through the system or by altering the length of the membrane. However, sufficient air flow must be required to ensure that the gas in front of the membrane is well mixed. The flow rates of oxygen and nitrogen across the membrane are determined by the difference in the partial pressures of each gas on the feed and permeate sides. Since the concentration of each gas changes over time, the mole flows are time dependent. Using Eqs. (1–3) and the ideal gas relation $p_\gamma/p = X_\gamma$, the mole flows of oxygen and nitrogen obey the equations

$$\frac{dn_{1f}}{d\tau} = \alpha \left(X_{1p} - X_{1f} \frac{p_1}{p_0} \right) = -\frac{dn_{1p}}{d\tau} \quad (4)$$

$$\frac{dn_{2f}}{d\tau} = \left((1 - X_{1p}) - (1 - X_{1f}) \frac{p_1}{p_0} \right) = -\frac{dn_{2p}}{d\tau} \quad (5)$$

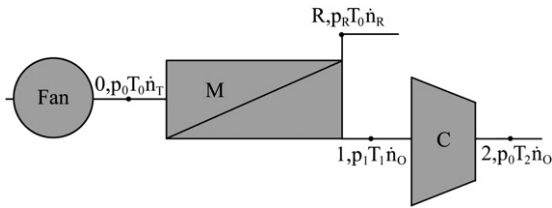


Fig. 2. Simple Membrane Process with a Vacuum Pump.

In Eqs. (4) and (5) n_{1f} , n_{1p} , n_{2f} and n_{2p} represent the time-dependent mole numbers—made dimensionless with the initial amount n_T —of the feed and permeate streams of O_2 (component 1) and N_2 (component 2), respectively. Furthermore, p_1 and p_0 are the total gas pressures on both sides of the membranes, and X_{1f} and X_{1p} are the time-dependent molar concentrations of oxygen on the feed and permeate sides,

$$X_{1p} = \frac{n_{1p}}{n_{1p} + n_{2p}} \quad (6)$$

$$X_{1f} = \frac{n_{1f}}{n_{1f} + n_{2f}} = \frac{(n_1 - n_{1p})}{(n_1 - n_{1p}) + (n_2 - n_{2p})} \quad (7)$$

Solutions to Eqs. (4) and (5) requires the initial conditions for n_{1f} and n_{2f} (and thus X_{1f}), which are given by the composition of air, $n_{1f}(\tau = 0) = X_{1f}(0) = 0.21$, and $n_{2f}(0) = X_{2f}(0) = 0.79$.

Moreover, for the initialization of our numerical solution of the equations, we require the initial composition $X_{1p}(\tau = 0)$ of the enriched gas on the permeate side of the membrane. This is found by defining X_{1p} at an infinitesimal time Δt and evaluating the equation as $\Delta t \rightarrow 0$.¹ Equations (4) and (5) are then substituted producing the equation

$$X_{1p}(\tau = 0) = \frac{\frac{dn_{1p}}{d\tau}}{\frac{dn_{2p}}{d\tau} + \frac{dn_{1p}}{d\tau}} = \frac{\alpha(X_{1p} - X_{1f} \frac{p_1}{p_0})}{(1 - X_{1p}) - (1 - X_{1f}) \frac{p_1}{p_0} + \alpha(X_{1p} - X_{1f} \frac{p_1}{p_0})} \quad (8)$$

The above equation must be solved for X_{1p} . This can easily be done as the initial values for α , p_1 , p_0 and X_{1f} are all known [14].

With $X_{1p}(\tau = 0)$ known for a given selectivity and pressure, the initial amounts of each component that pass through the membrane can be found relative to one another. For the numerical solution, the initial amount of moles of oxygen, n_{1p} , is set to a small value of 0.001 to simulate the initial flow of oxygen across the membrane. This value is then used in conjunction with the initial permeate concentration to find the initial amount of nitrogen.

$$n_{1p}(\tau = 0) = 0.001 \quad (9)$$

$$n_{2p}(\tau = 0) = \left(\frac{n_{1p}(\tau = 0)}{X_{1p}(\tau = 0)} - 1 \right) \quad (10)$$

Using these initial conditions, Eqs. (4) and (5) are solved by means of the mathematical software package Mathematica[®], to give the mole numbers of oxygen and nitrogen on both sides of the membrane as a function of dimensionless permeation time τ . The

concentrations of oxygen and nitrogen on the feed and permeate sides can then be found as a function of permeation time. The resulting graphs produced for a selectivity of 8 and a pressure ratio of 3 across the membrane are shown in Fig. 3, which allows for further understanding of the effect of the membrane.

As can be seen from the figure, the initial concentration of oxygen on the permeate side is higher ($\sim 45\%$) than on the feed side ($\sim 21\%$) due to the higher permeability for O_2 . As time progresses, though, the oxygen concentration on the permeate side will slowly decrease. If the gases are allowed to permeate through the membrane for an infinite amount of time, the concentrations on the feed and permeate side will eventually become equal. It is important to note that even though the oxygen concentration is high at low permeation times, the corresponding actual amount of oxygen transported through the membrane is small, as can be seen in Fig. 3 right. Thus, a compromise must be made between the desired concentrations of the permeate stream and the amount of product.

Creation of the pressure difference between the feed and permeate sides is the only work requirement for membrane separation. This can be done by the arrangements shown in Figs. 1 and 2, respectively. To determine the specific work per mole passing through for a compressor and a turbine, we assume that both devices operate on irreversible adiabatic processes with isentropic efficiency η [15]. The required pressures are relatively small, temperatures vary only slightly, and we can assume constant specific heats for the involved gases. Then, the compressor and turbine work are

$$\bar{w}_{\text{comp}} = -\frac{kR_u T_0}{\eta(k-1)} \left(\left(\frac{p_1}{p_0} \right)^{\frac{k-1}{k}} - 1 \right) \quad (11)$$

$$\bar{w}_{\text{turb}} = -\frac{\eta k R_u T_R}{k-1} \left(\left(\frac{p_0}{p_R} \right)^{\frac{k-1}{k}} - 1 \right) \quad (12)$$

Here, $k = 1.4$ and is the ratio of specific heats, R_u is the universal gas constant, $T_0 = 298$ K is the temperature of the environment, $p_0 = 101.3$ kPa is the atmospheric pressure, p_1 is the pressure after the compressor, p_R is the pressure at the turbine inlet and T_R is the gas temperature at the turbine inlet.

The compressor and turbine are fully reversible if $\eta = 1$. If the isentropic efficiency is less than 100% (i.e. $\eta < 1$) then work is lost through irreversibilities. The amount of overall work loss to these irreversibilities increases with the amount of gas processed by the devices.

The vacuum pump work is approximated as an adiabatic compressor. This arrangement also requires a blower to keep fresh, undepleted air flowing past the membrane. The specific work per mole passing through for the blower is calculated as the change in kinetic energy of the air and the additional energy required because of pressure loss due to friction in the pipe.

$$\bar{w}_{\text{blower}} = -\frac{1}{2\eta} (v_f^2 - v_i^2) M_{O_2} - \frac{kR_u T_0}{\eta(k-1)} \left(\left(\frac{p_0}{p_0 - p_{\text{fric}}} \right)^{\frac{k-1}{k}} - 1 \right) \quad (13)$$

Here, v_f is the final air velocity, v_i is the initial air velocity and p_{fric} is the pressure loss due to friction. The pressure loss from friction is calculated using fluid mechanics with assumptions of feed pipe dimensions and roughness.

The total work required by the membrane process depends upon the mole flow of air through the system. As seen in Fig. 1, the mass flow through the compressor is larger than through the turbine as the compressor processes all air, while the turbine only expands the waste gas. Similarly, for the vacuum pump of Fig. 2, the blower processes all air, while the vacuum pump only processes the

¹ See Appendix A.1 for a detailed derivation of Eq. (8).

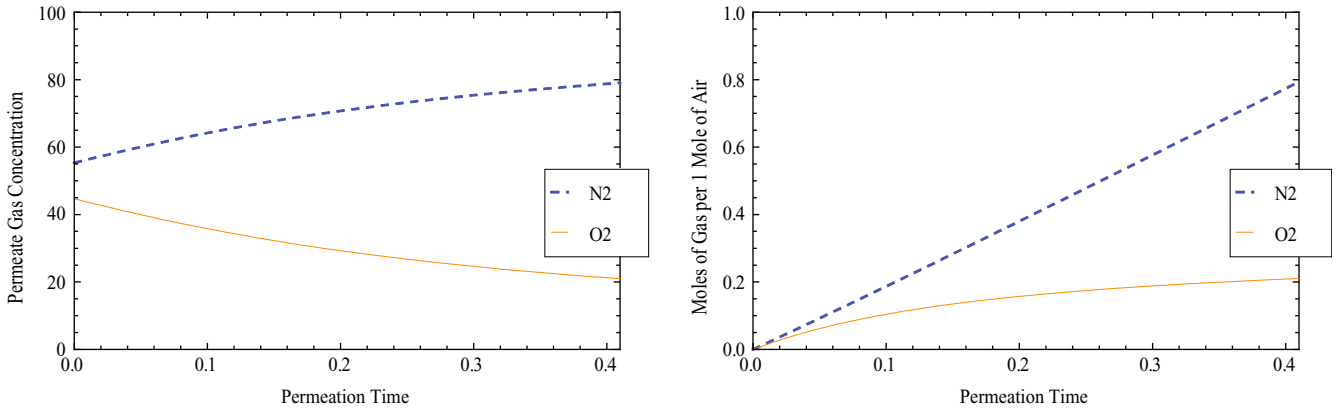


Fig. 3. O₂ and N₂ Gas Concentrations on the permeate side (left) and Moles of Gas Absorbed through the membrane (right) as a Function of Permeation Time.

air that passes through the membrane. The total work per unit mass of O₂ in the enriched gas for the compressor/turbine (ct) and vacuum pump (vp) systems are

$$W_{\text{mem,ct}} = \left(\bar{w}_{\text{comp}} + \left(\frac{\dot{n}_R}{\dot{n}_T} \right) \bar{w}_{\text{turb}} \right) \left(\frac{\dot{n}_T}{\dot{n}_{1p}} \right) \left(\frac{1}{M_{\text{O}_2}} \right) \quad (14)$$

$$W_{\text{mem,vp}} = \left(\bar{w}_{\text{blower}} + \left(\frac{\dot{n}_O}{\dot{n}_T} \right) \bar{w}_{\text{comp}} \right) \left(\frac{\dot{n}_T}{\dot{n}_{1p}} \right) \left(\frac{1}{M_{\text{O}_2}} \right) \quad (15)$$

The factor \dot{n}_T/\dot{n}_{1p} represents the conversion from moles of incoming gas to moles of oxygen outputted. As can be seen in Fig. 3, the moles of oxygen outputted per mole of incoming gas increases with permeation time while the concentration of oxygen decreases over time. A balance must be found between the desired concentration of the product and the work required to produce a certain amount of product.

The total number of moles flowing through the system is defined as $\dot{n}_T = \gamma n_T$ where n_T is the unit amount of air considered in the above calculations, and γ is the rate at which this amount enters the system. Variables \dot{n}_O and \dot{n}_R are the mole flows of the oxygen rich gas and the waste gas respectively and are defined as:

$$\dot{n}_O = \dot{n}_{1p}(\tau) + \dot{n}_{2p}(\tau) = \gamma(n_{1p}(\tau) + n_{2p}(\tau)) \quad (16)$$

$$\dot{n}_R = \dot{n}_1 - \dot{n}_{1p}(\tau) + \dot{n}_2 - \dot{n}_{2p}(\tau) = \gamma(n_1 - n_{1p}(\tau) + n_2 - n_{2p}(\tau)) \quad (17)$$

Irreversibilities of the membrane process occur in the compressors, turbines, blowers and the membrane itself. Work is lost due to the inefficiencies of the compressor, turbine and blower. A large amount of work is also lost due to friction between the membrane and the permeating gas. As the gas passes through the membrane, it expands to atmospheric pressure from the high pressure after the compressor. Thus, the compression work cannot be recovered or used in any regeneration process—it is irreversibly lost to friction.

As is evident from Fig. 3, selective membranes cannot achieve the high purities needed for the oxy-fuel process. They can however be used produce oxygen-enriched air at a relatively small energy cost [16]. There is also an optimum balance between membrane selectivity and the individual permeability of each component which determines membrane thickness, permeation time and surface area needed for a desired separation. Additional separation systems are required to achieve the high purities needed by that of the oxy-fuel combustion process [10].

Though a relatively new technology, polymeric membranes have begun to peak in performance and, based upon current available materials, approach the limit noted by Robeson [17]. This limit is a logarithmic curve that relates the maximum permeability

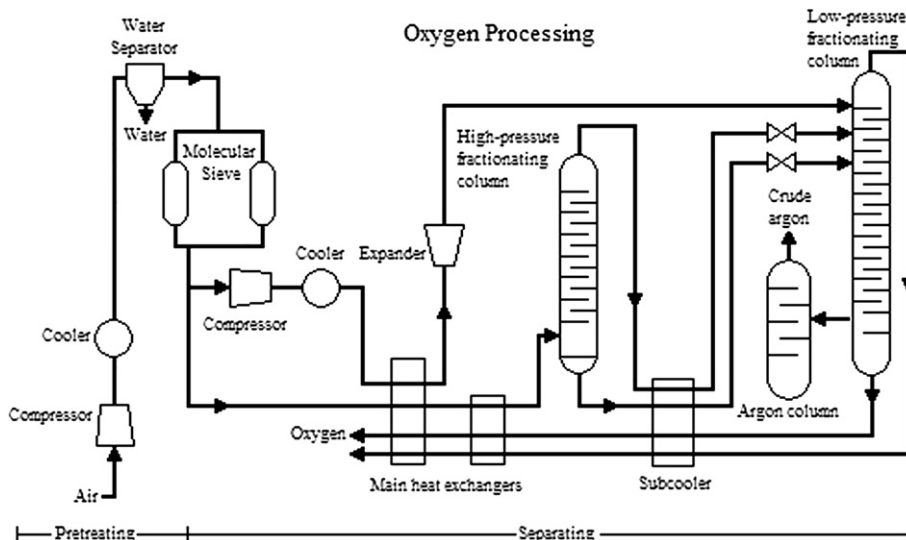


Fig. 4. Actual Cryogenic Distillation System using the Linde Process [20].

for a given selectivity. Robeson argues that advances in materials will continue to increase this limit and are required for large leaps in the technology [18].

2.2. Cryogenic distillation

Cryogenic distillation is a technology that has been around since the early 1900s when the Linde process was developed [15]. Gases such as oxygen and nitrogen, the primary constituents of air, decrease in temperature and condense when throttled because they have a positive Joules–Thompson coefficient. By controlling how much the temperature decreases through pressurizing and throttling the air, oxygen and nitrogen can be separated by phase as they have different boiling temperatures.

The cryogenic distillation process can be very complex in practice, but here a simplified model that approximates the actual process is used for analysis. Ambient air which contains approximately 21% oxygen by volume is first pre-cooled by the cycle's product (oxygen) and waste gases (nitrogen and argon). The air is then compressed in a multistage process to 650 kPa. It is subsequently throttled causing it to cool to low temperatures and liquefy. Oxygen and nitrogen are then separated by phase in a fractional distillation column. While the oxygen settles to the bottom of the column as liquid, the nitrogen boils and is taken out of the top of the column. The contents are then sent to a low pressure distillation column to increase the oxygen purity. The end result is oxygen with a purity greater than 99% which can be used in oxy-fuel combustion. Both the product and waste gases are at temperatures close to their respective boiling points. These low temperature gases are used to pre-cool the input gases thus lowering the work required for the initial compression [20]. One configuration of an actual cryogenic distillation process is shown in Fig. 4.

Though the cryogenic process involves several compressors and turbines, the overall work for the entire system can be accurately represented by the work required to compress the incoming air to 650 kPa. This compression is done in two-stages with intercooling, see Fig. 5.

To compute the specific work per mole of incoming gas for this two-stage compression we again consider adiabatic irreversible compression with isentropic efficiency η , so that [15]

$$\bar{w}_{\text{cryo}} = -\frac{2kR_u T_{\text{cryo}}}{\eta(k-1)} \left(\left(\frac{p_m}{p_0} \right)^{\frac{k-1}{k}} - 1 \right) \tag{18}$$

All of the variables for the above two-stage compression are constants. T_{cryo} is the input temperature of the air (taken as 270 K after pre-cooling), η is the compressor efficiency (assumed to be 90%), and p_m is the intermediate pressure of the two compressors. This intermediate pressure is chosen such that the minimum amount of work is used in compression. The intermediate pressure can be found using the equation below pending that both compressors have the same isentropic efficiency, which is assumed to be the case in this analysis.

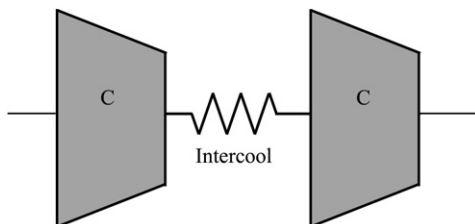


Fig. 5. Work Equivalent of a Simple Cryogenic Process with Two-Stage Compression.

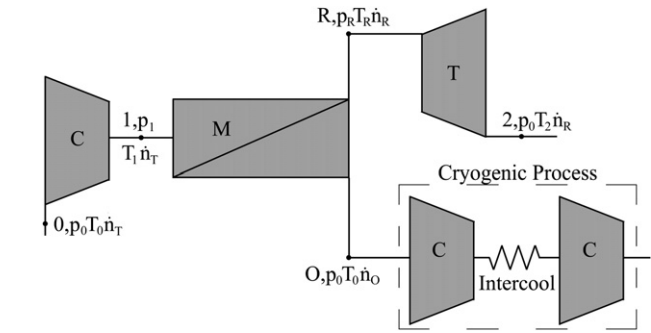


Fig. 6. Process Flow Diagram for Case 1: Simple Compressor and Turbine.

$$p_m = (P_{\text{cryo}} p_0)^{\frac{1}{2}} \tag{19}$$

P_{cryo} is the final pressure of 650 kPa. Converting this cryogenic work from moles of incoming gas to work per mass of oxygen produced

$$w_{\text{cryo}} = \bar{w}_{\text{cryo}} \left(\frac{\dot{n}_T}{\dot{n}_{1p}} \right) \left(\frac{1}{M_{O_2}} \right) \tag{20}$$

The factor \dot{n}_T / \dot{n}_{1p} represents the conversion from moles of incoming gas to the moles of oxygen in the incoming gas. For ambient air this is equal to 1 mol of air for every 0.21 mol of O_2 . The molar mass of oxygen converts from moles to grams of oxygen.

Cryogenic distillation uses a large amount of energy due to irreversibilities that arise in the process, where the amount of energy lost depends on the size of the production. For large scale production the losses are relatively low (compared to smaller processes) and the gas needs to be compressed to only about 650 kPa. For small to medium scale applications the irreversibilities are more prominent and the air must be compressed to higher pressures to achieve the desired low temperatures for separation. Major irreversible losses occur due to the inefficiencies of the compressors, heat dissipation of the gases, unrestrained expansion in the throttle, and heat loss to the environment. Most importantly, in smaller systems the surface/volume ratio is larger, and thus the relative amount of heat loss is larger as heat from the environment creeps into the smaller volume of cooled gases.

Cryogenic distillation is almost a fully mature technology with future improvements only to be expected from improved turbine, compressor and heat exchanger efficiencies. For the large scale production of several thousand tons of oxygen needed by the oxy-fuel process, the current work requirement is 220 kWh/t n O_2 based upon a report by Foster Wheeler [21] and is 245 kWh/t n O_2 from Hong et al. [22]. This value varies significantly depending upon the purity desired. This paper will assume a baseline of 220 kWh/t n O_2 as it is comparable to the basic calculation in Equation 18 and it

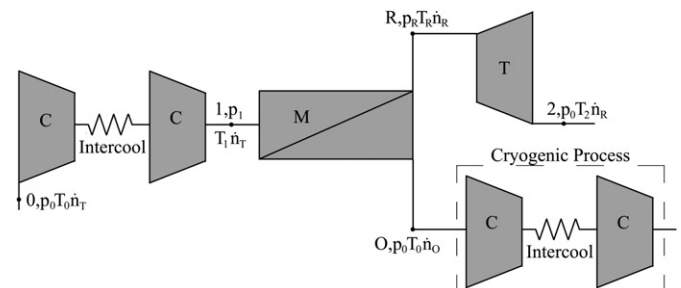


Fig. 7. Process Flow Diagram for Case 2: Two-Stage Compressor and Turbine.

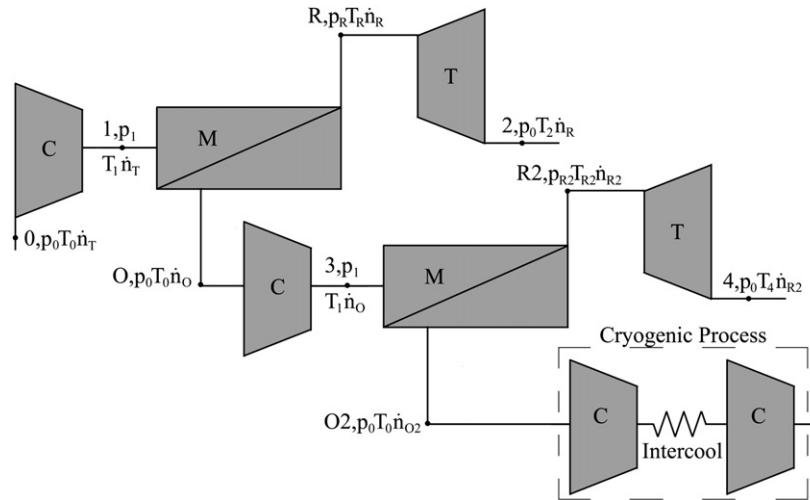


Fig. 8. Process Flow Diagram for Case 3: Two Subsequent Membrane Separations with Compressors and Turbines.

provides a more competitive estimate for comparison. However, the work requirement also varies depending on production volume. For production between 500 and 1000 tons of oxygen the work required by cryogenic distillation lies between 340 and 280 kWh/tn O₂ [23]. The increase is due to increased irreversibilities of the process at smaller scales as discussed above. With increased irreversibilities it is necessary to increase the pressure of the incoming gas for separation which requires more work.

Regardless of the size of the operation, a large amount of the work required is due to the compression of nitrogen in the air. Since air is 21% O₂ by volume, the production of 1 ton of oxygen requires the compression of 5 ton of air. A feed of oxygen enriched gas into the Linde process requires compression of a smaller amount of gas, and therefore will reduce the irreversible losses, since these are proportional to the amount of feed.

3. Hybrid membrane and cryogenic process

3.1. Process methodology

It is our hypothesis that a combination of membrane and cryogenic technology can be used to effectively produce high purity oxygen at less than the industry standard of 220 kWh/tn O₂ for a large amount of product. A variety of systems are considered to

test this hypothesis. The hybrid systems will also be tested against medium scale cryogenic separation that requires 320 kWh/tn O₂.

By evaluating the cryogenic process it can be seen that a large amount of work is required to compress the nitrogen in the air. If the concentration of oxygen in the cryogenic feed gas was 42%, the work required in the cryogenic stage would effectively be one half of the current amount, since only half the volume of gas would need to be compressed to obtain the same amount of product. Similarly, if the feed gas was 63% O₂, the work would be one third as much. Instead of compressing 5 ton of air for every 1 ton of oxygen produced, only half or a third of the amount of O₂-enriched air would be required for the same amount of product.

The goal of the hybrid system is to produce high purity oxygen using less work than the current standard. In other words the work required by the membrane and cryogenic processes together should be less than for the cryogenic process alone. Even though the membrane process adds additional work, the work required for the cryogenic process is decreased because oxygen enriched gas is used.

3.2. Design permutations

The general process of the design employs passing air by a selective O₂/N₂ permeable membrane that has a pressure difference induced across it. This will cause a flux of oxygen and nitrogen

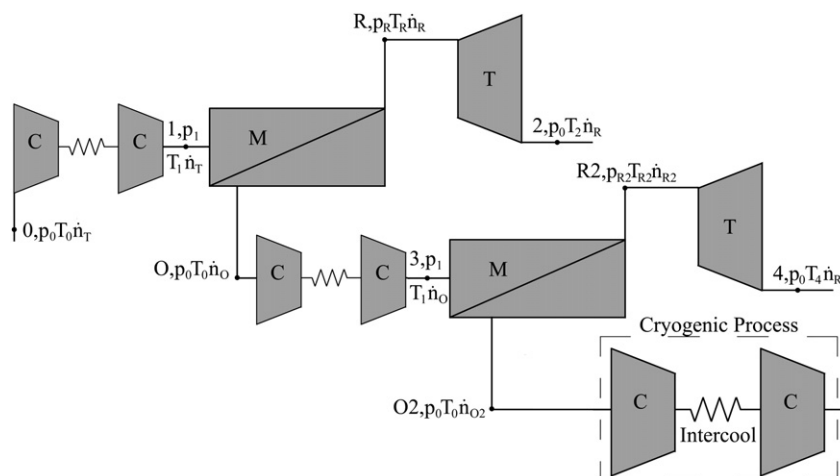


Fig. 9. Process Flow Diagram for Case 4: Two Subsequent Membrane Separations with Two-Stage Compressor and Turbine.

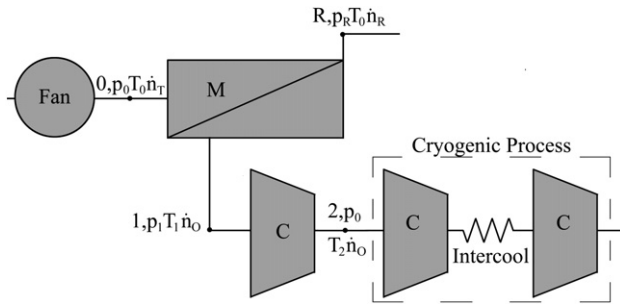


Fig. 10. Process Flow Diagram for Case 5: Vacuum Pump.

through the membrane. Depending on the membrane selectivity, the oxygen flux will be larger than the nitrogen flux producing oxygen rich air on the permeate side. The oxygen concentration is dependent upon several factors such as the pressure ratio across the membrane, permeability and selectivity.

This oxygen rich air then enters the cryogenic distillation stage. Since the oxygen concentration is larger than 21%, the work required per unit oxygen for the cryogenic process will be less than the standard process. Several configurations and parameters will be employed to investigate whether or not the work required in the membrane stage is less than the work saved in the cryogenic stage.

Use of an O₂/N₂ permeable membrane and a cryogenic distillation process allows for a variety of configurations. These include using a compressor-turbine arrangement, a vacuum pump arrangement, two-stage compression and two-stage membranes. All configurations are analyzed using Eqs. (1–20) for determining the time-dependent mol flux through the membrane and the overall work required per ton of oxygen produced.

3.2.1. Case 1: simple compressor-turbine process

In the simple compressor-turbine process air is compressed to a specified pressure p₁ then sent to an O₂/N₂ permeable membrane as shown in Fig. 6. Oxygen and nitrogen pass through the membrane creating oxygen rich gas on the permeate side. While the oxygen rich gas travels to the cryogenic system, the nitrogen rich waste gas is sent through a recovery turbine. The membrane is considered to be adiabatic and the turbine expands the pressurized gas to atmospheric pressure. The total work for the process is:

$$w_{Case1} = \left[\bar{w}_{comp} + \left(\frac{\dot{n}_R}{\dot{n}_T} \right) \bar{w}_{turb} + \left(\frac{\dot{n}_O}{\dot{n}_T} \right) \bar{w}_{cryo} \right] \left(\frac{\dot{n}_T}{\dot{n}_{1p}} \right) \left(\frac{1}{M_{O_2}} \right) \quad (21)$$

3.2.2. Case 2: two-stage compressor and turbine

Similar to the previous configuration, a compressor is coupled with a turbine, but instead of using one compressor, two-stage compression is used (see Fig. 7) to lower the amount of work required by compression to p₁ and the temperature of the gas in the

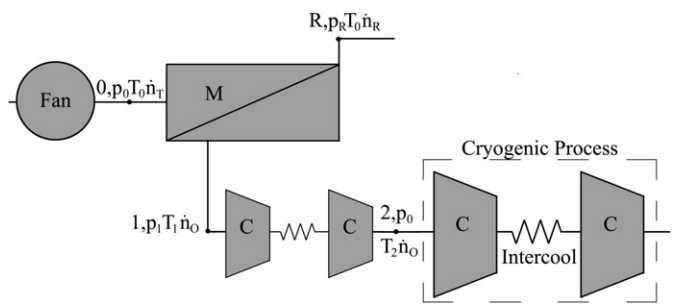


Fig. 11. Process Flow Diagram for Case 6: Two-Stage Vacuum Pump.

membrane. While this benefits membranes with a lower maximum operating temperature, the turbine inlet temperature will be lower, resulting in less work recovery per unit of air. The resulting work is found using Eq. (21).

3.2.3. Case 3: two subsequent membrane separations with compressors and turbines

Case 3 is shown in Fig. 8. Using two membranes increases the oxygen concentration more than the previous designs, but also adds another compressor and turbine pair. The cryogenic work will be decreased while the membrane work is increased. This may be desirable in low product situations, if the cryogenic system needs to be small, and providing extra work is not an issue. The air flow through the second compressor is reduced as the air has already passed through one membrane. Addition of a second membrane adds more terms in the equation for the total work required by Case 3:

$$w_{Case3} = \left[\bar{w}_{comp1} + \left(\frac{\dot{n}_R}{\dot{n}_T} \right) \bar{w}_{turb1} + \left(\frac{\dot{n}_O}{\dot{n}_T} \right) \bar{w}_{comp2} + \left(\frac{\dot{n}_{R2}}{\dot{n}_T} \right) \bar{w}_{turb2} + \left(\frac{\dot{n}_{O2}}{\dot{n}_T} \right) \bar{w}_{cryo} \right] \left(\frac{\dot{n}_T}{\dot{n}_{1p2}} \right) \left(\frac{1}{M_{O_2}} \right) \quad (22)$$

3.2.4. Case 4: two subsequent membrane separations with two-stage compressor and turbine

A combination of Case 2 and Case 3, the two-stage membrane and two-stage compressor set-up in Fig. 9 aims to meet certain needs. If the membrane has a maximum temperature requirement, two-stage compressors help to reduce the membrane temperature. The two-stage membrane process attempts to enrich the oxygen as much as possible to reduce the work required by the cryogenic stage. The formula used for calculating the total work is identical to Eq. (22).

3.2.5. Case 5: vacuum pump arrangement

A variant of the compressor-turbine arrangement, the vacuum pump arrangement in Fig. 10 utilizes only one compressor. Instead of creating a high pressure on the feed side of the membrane, low pressure is induced on the permeate side. This configuration has the advantage that a smaller amount of gas is compressed than in the previous arrangements, since the vacuum pump only processes the enriched air that permeates through the membrane instead of all incoming air. While this reduces the size of the required compressor, a blower is required to feed fresh air past the membrane which adds work and irreversibility to the system. Due to the smaller pressures, the gas densities are lower, thus the size of the membrane system must be larger. The total work required is:

$$w_{Case5} = \left(\bar{w}_{blower} + \left(\frac{\dot{n}_O}{\dot{n}_T} \right) (\bar{w}_{comp} + \bar{w}_{cryo}) \right) \left(\frac{\dot{n}_T}{\dot{n}_{1p}} \right) \left(\frac{1}{M_{O_2}} \right) \quad (23)$$

3.2.6. Cases 6 and 7: two-stage vacuum pump, and two subsequent membrane separations with vacuum pump

The final two configurations, depicted in Fig. 11 and Fig. 12, add a second vacuum pump and a second membrane, respectively. The total work is the summation of the vacuum pumps, blowers and cryogenic stages. The total work for Case 6 can be calculated using Eq. (23) while the work for Case 7 is calculated from

$$w_{Case7} = \left(\bar{w}_{blower1} + \left(\frac{\dot{n}_O}{\dot{n}_T} \right) (\bar{w}_{comp1} + \bar{w}_{blower2}) + \left(\frac{\dot{n}_{O_2}}{\dot{n}_T} \right) (\bar{w}_{comp2} + \bar{w}_{cryo}) \right) \left(\frac{\dot{n}_T}{\dot{n}_{1p2}} \right) \left(\frac{1}{M_{O_2}} \right) \quad (24)$$

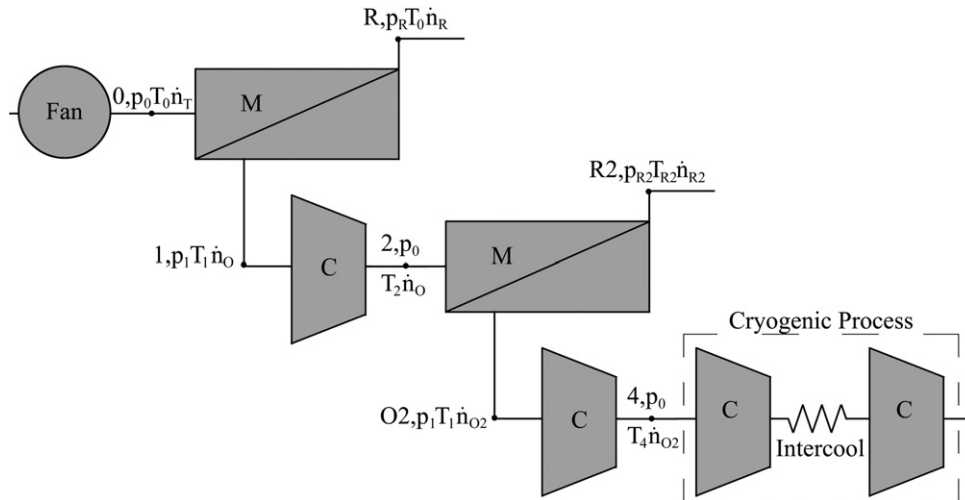


Fig. 12. Process Flow Diagram for Case 7: Two-Stage Membrane Vacuum Pump.

4. Results

4.1. Large scale (1000's of tons of oxygen/day)

All seven configurations are compared to each other, and to the base value for cryogenic separation of 220 kWh/tn O₂. The

configuration requiring the least amount of work, Case 6, is incorporated into the current oxy-fuel combustion model to evaluate its impact. The only system parameters are the membrane selectivity and the pressure ratio across the membrane. While the pressure ratio can be controlled and optimized to minimize the work required by compressors and turbines, here all systems use

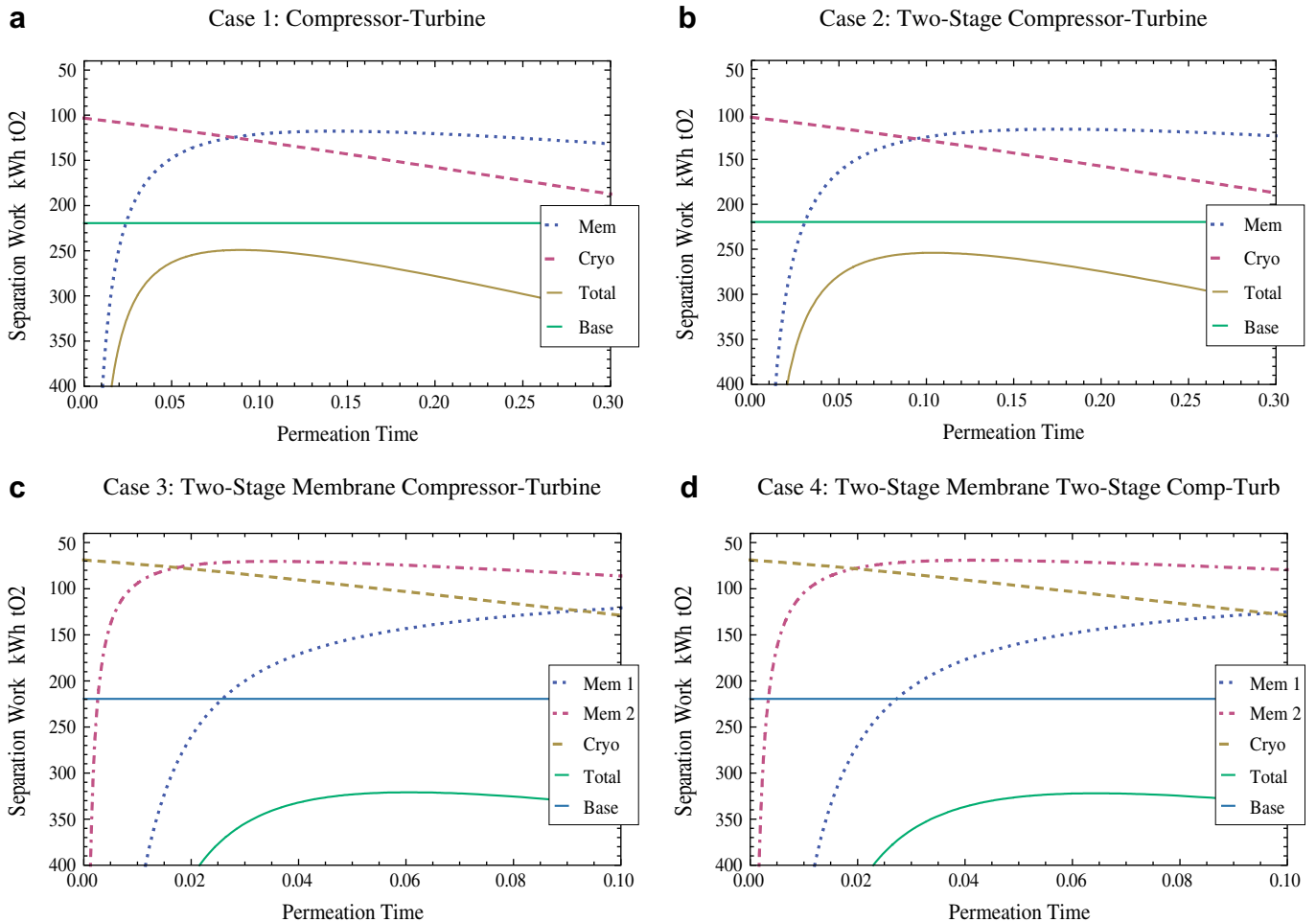


Fig. 13. Separation Work for Cases 1–4 with Selectivity of 8, Pressure Ratio of 3 and η of 90%.

the same pressure ratio of 3 to provide consistent results. The membrane selectivity is a property of the membrane, however, and is chosen as $\alpha = 8$ which is the value for some of the better existing membranes [18] [19]. Higher selectivities decrease the separation work while lower selectivities increase the separation work.

For the two-stage membrane systems, the permeation time for the first membrane is chosen such that the overall work is minimized. This is done by analyzing the system as if the second membrane did not exist and finding the permeation time which requires a minimum amount of work. The permeation time for the second membrane is then allowed to vary to witness its effect on the work over time.

The effect of varying the membrane selectivity is examined for both variants of the design. The impact of using waste heat to increase the temperature of the gas entering the turbine and the impact of isentropic efficiencies are also investigated.

The subsequent plots show the total work required for separation over the dimensionless permeation time τ , *i.e.* the time that the feed air has contact with the membrane. The work required by the membrane and the cryogenic stages is shown separately to emphasize how each stage varies over time. The resulting graphs for Separation Work vs. Permeation Time are shown in Fig. 13 for the compressor turbine arrangements and Fig. 14 for the vacuum pump arrangements. Here, the membrane work is the total of all compressors and turbines, and the cryogenic work is the work for the two-stage compression to 650 kPa for the hybrid process, while the base value is the work required for a cryogenic system by itself. The total work is the addition of all blower, membrane and cryogenic work.

This total value is compared to the base value. If the total is above the base value the design shows potential to be an improvement over the current standard.

As previously demonstrated in Fig. 3, low permeation times produce a high oxygen concentration on the permeate side of the membrane, but the mass flow of oxygen is very low. This means that in the compressor-turbine configurations at low permeation times the compressor has to compress a very large amount of air to produce a small amount of product. High permeation times produce a large mass flow but result in lower oxygen concentrations behind the membrane, which is the entry to the cryogenic stage; this leads to high amounts of work for the cryogenic stage.

As seen in Fig. 13, due to smaller amount of gas processed, the cryogenic work is substantially decreased from the original 220 kWh/t_n O₂. As permeation time increases, the cryogenic work slowly increases toward the base value, since, as time progresses, the feed concentration of oxygen decreases, as more nitrogen passes through per molecule of oxygen (Fig. 3). As the partial pressure of oxygen on the feed side decreases, the oxygen flux through the membrane decreases. The initial concentration of oxygen through the membrane is thus the highest and would result in the least amount of cryogenic work.

The work required by the membrane stage is a maximum at a permeation time of zero. When the membrane first operates, the number of molecules which permeate through is small, even though the oxygen concentration is high. This means that at short permeation times, to get 1 unit product of oxygen, the compressor needs to compress a large amount of air. Since the compressor and the recovery turbine are irreversible, a large amount of work is lost due to the large air flow required. Therefore, as will be seen, for each case the minimum amount of work for the process is a compromise between the optimum cryogenic and membrane scenarios.

For the vacuum pump arrangements, a fan, or blower, is required to force air past the membrane. If no fan is present the air would be stagnant on one side of the membrane preventing continuous

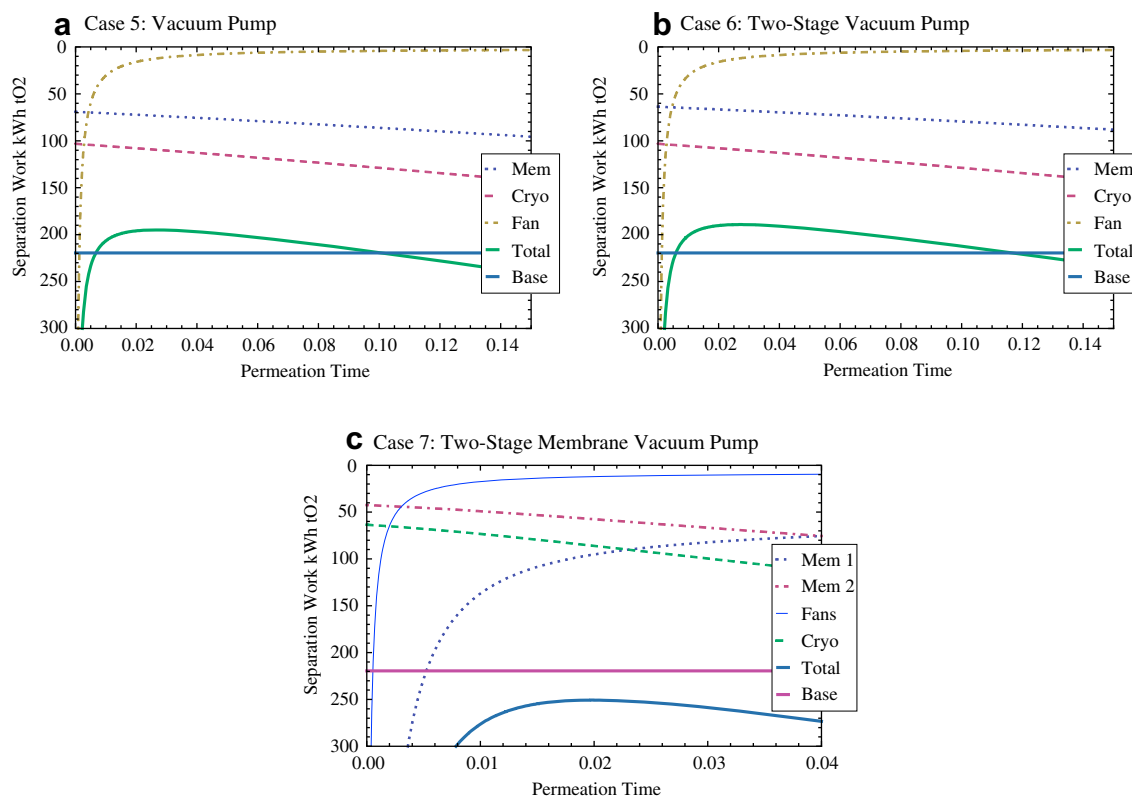


Fig. 14. Separation Work for Cases 5–7 with Selectivity of 8, Pressure Ratio of 3 and η of 90%.

operation. The fan also helps to ensure thorough mixing of the gas replacing oxygen depleted air with fresh air. Incorporated into the blower work is the small amount of compression work needed to counteract friction loss in the pipe. This friction loss is conservatively approximated through fluid mechanics and is dependent upon the pipe dimensions, the air velocity and the friction factor of the membrane. Similar to the compressors, the work for the fan varies depending upon how much oxygen is absorbed through the membrane. The blower work is small in comparison to the compressor work except at low permeation times when the blower work will be significantly higher due to the small amount of gas that passes through the membrane. This implies that the blower has to provide a large amount of air.

The separation work for the vacuum pump arrangements is shown in Fig. 14. The work required for both the membrane and the cryogenic systems benefit the most from low permeation times. This is expected as both the vacuum pump and cryogenic compressors only process air that passes through the membrane. Again, at low permeation times the oxygen concentration is higher resulting in less work per unit oxygen.

The effect of varying the membrane selectivity, adding waste heat to the turbine gas and using different isentropic efficiencies is investigated next, in Figs. 15–17. As can be seen from Fig. 15, selectivity plays a large role in the total work required for separation. Membranes with a selectivity of 4 have a significant disadvantage over higher selectivities with both Cases 2 and 6 falling well below the base value of 220 kWh/t_n O₂. Additionally, the reduction in separation work between a selectivity of 8 and 12 is small in comparison to the difference between selectivities of 4 and 8.

The addition of heat to the turbine inlet for Case 2, shown in Fig. 16, makes a significant difference in regards to the total work required. A difference of over 40 kWh/t_n O₂ can be seen from an increase in temperature of 80 K allowing for the total work to be an improvement over the base value.

An increase in isentropic efficiencies of the compressors and turbines also benefits the hybrid design as can be seen from Fig. 17. At an efficiency of 85%, for all compressors and turbines in Case 1, the hybrid design requires 50 kWh/t_n O₂ more work than the base value at the same efficiency. At 95% efficiency, however, the hybrid design has a minimum work almost equal to the base value. This emphasizes the importance and effect that increased efficiencies can have on a design due to decreased irreversibilities.

Plotted in Fig. 18 is the total work for Cases 1–4 (left) and Cases 5–7 (right). None of the compressor-turbine arrangements, Cases 1–4, surpass the base value. The two-stage membranes of Cases 3 and 4 are especially poor while Cases 1 and 2 give similar results close to 250 kWh/t_n O₂. For the vacuum pump arrangements both Case 5 and 6 are above the base value while the two-stage membrane, Case 7, falls below the current standard.

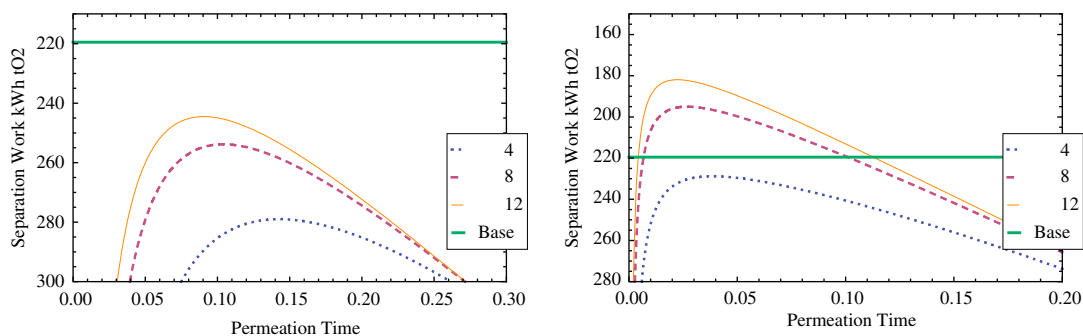


Fig. 15. Total Work for Case 2 (left) and Case 6 (right) with Varying Selectivities.

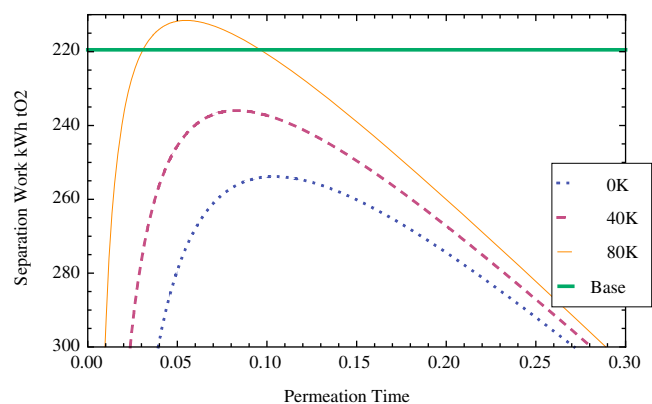


Fig. 16. Total Work for Case 2 with Heat Addition to Turbine Air.

Since Case 6 requires the least amount of work at approximately 190 kWh/t_n O₂ for a given permeation time, the effect of this hybrid air separation unit on the oxy-fuel system is analyzed. From Kvamsdal et al. [7] the impact to the efficiency of a gas turbine combined cycle plant from oxygen production is 8.8%. Approximately 6.4% is from the production of oxygen while the remaining 2.4% is required for compression in preparation for combustion. As discussed in Section 5.2 the hybrid process is substitutable to the cryogenic separation unit in terms of overall integration to the oxy-fuel process. Thus for an oxy-fuel plant originally expected to produce oxygen at 220 kWh/t_n O₂, Case 6 reduces the work penalty from 6.4% to 5.5%. The work penalty for oxygen production and compression is similarly noted in Davison et al. [24] to be approximately 8% for natural gas combined cycle plants.

4.2. Small scale (100's of tons of oxygen/day)

Though the intended goal of the hybrid system is large oxygen production for the oxy-fuel process, the idea has opportunities in smaller production applications. Operations which require between 500 and 1000 tons of oxygen per day currently require between 340 and 280 kWh/t_n O₂ using cryogenic distillation. This increased work demand is due to the additional losses and inefficiencies associated with smaller production.

For comparison of the hybrid system to the cryogenic process for smaller production, the work required for the cryogenic process alone is set as 320 kWh/t_n O₂, the value for a production of approximately 700 t_n O₂/day [23]. This requires a compression in the cryogenic stage to 1320 kPa, up from the 650 kPa for large scale. The cryogenic stage in the hybrid design is also compressed to this pressure. The membrane stage, however, is independent of the

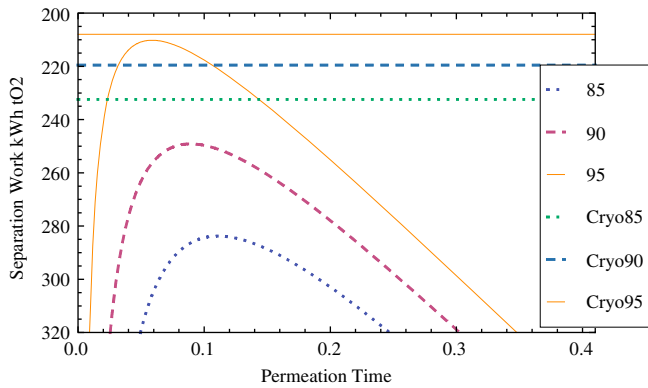


Fig. 17. Total Work for Case 1 with Different Efficiencies.

increased cryogenic pressure and the work is the same as for large scale production.

Graphs for the Separation Work VS Permeation Time for small scale production are shown in Fig. 19 for Case 1 and Case 6. The work required by the membranes and blowers is identical for small and large scale production. Compared to large scale processes, the cryogenic work for both the hybrid and standard design are significantly increased. Both Case 1 and 6 show improvement against the small scale benchmark of 320 kWh/tn O_2 .

The total work for Cases 1–4 is plotted in Fig. 20 (left) for comparison while the total work for Cases 5–7 is in Fig. 20 (right). In the compressor-turbine arrangements both Case 1 and 2 surpass the base value while Case 3 and 4 are below the current standard. In the vacuum pump arrangements all three cases supercede the base value with Case 6, the two-stage vacuum pump, requiring the least amount of energy at 240 kWh/tn O_2 . The amount of work required by Case 7, the two-stage membrane, is approximately 290 kWh/tn O_2 .

5. Discussion

5.1. Evaluation of hybrid air separation unit

For comparison of the different configurations, the total work required for large scale separation of each configuration is shown in Fig. 18. By analyzing Fig. 13 through Fig. 20 several conclusions can be deduced about the hybrid membrane and cryogenic systems.

The first deduction relates to the benchmark of 220 kWh/tn O_2 currently required to produce oxygen in large quantities using the Linde process. Only the vacuum pump scenarios produce results that show a decrease in work requirements but only at small permeation times. The primary benefit, as seen in Fig. 14 a,b, is the relatively constant amount of work needed for the membrane stage

compared to the compressor-turbine configuration. From Fig. 15, however, it is important to note that the selectivity plays a deciding role in the total work required.

Another deduction is that any two-stage membrane system will require too much work to be practical in the separation of air. The work required for separation is large because of the small amount of product that comes out of the second membrane. A significant amount of oxygen that passes through the first membrane is discarded at the second membrane. When calculating the overall work for the system per unit mass of O_2 , the work done by the first compressor is dependent on how much oxygen permeates through the second membrane. Even though the oxygen concentration is high after the second membrane, the overall percentage of oxygen captured from the ambient (source) air is very low. Thus, the first membrane system has to process a lot of air in order to produce 1 ton of oxygen for the cryogenic stage. Recall, that the losses in the compressor-turbine assembly are proportional to the total amount of gas passing through.

Configurations that involve two-stage compression generally require more work than those with just one compressor, see Case 1 to Case 2 in Fig. 18 (left). In two-stage compression the compression work is significantly less but, since heat is rejected during inter-cooling, the recovery turbine produces substantially less work than in the single compressor case. For Case 5 and Case 6 in Fig. 18 (right), however, since no recovery turbine exists, it is more beneficial to use two-stage compression.

Membrane selectivity also plays a pivotal role in the energy required for separation. Fig. 15 compares the separation work for membrane selectivities of 4, 8, and 12. It can be seen that the work decreases for higher selectivities as oxygen permeates through the membrane much easier than nitrogen. It is also notable that the decrease in work associated with a selectivity of 8 compared to 4 is much larger than a selectivity of 12 compared to 8. This implies that, as the selectivity approaches high values, its benefit towards the system becomes smaller. Thus if extra cost or maintenance is required to produce a high selectivity membrane it may be more cost effective to use a membrane with a lower selectivity and take a larger energy penalty.

For the compressor-turbine arrangement the possibility of adding heat to the turbine inlet gas is investigated. This heat could come from any potential waste heat of the power plant. This may include cycling a pipe through the boiler, removing heat from the water after it goes through the steam turbine or heat from the flue gases. Heat should only be added to the stream if it can benefit the overall efficiency of the power plant. Otherwise one would remove heat that could be used elsewhere to facilitate the generation of power. For the compressor-turbine arrangement of Case 2, the effect of a different temperature at the turbine inlet can be seen in Fig. 16. Increasing the inlet temperature by 80 K allows for the

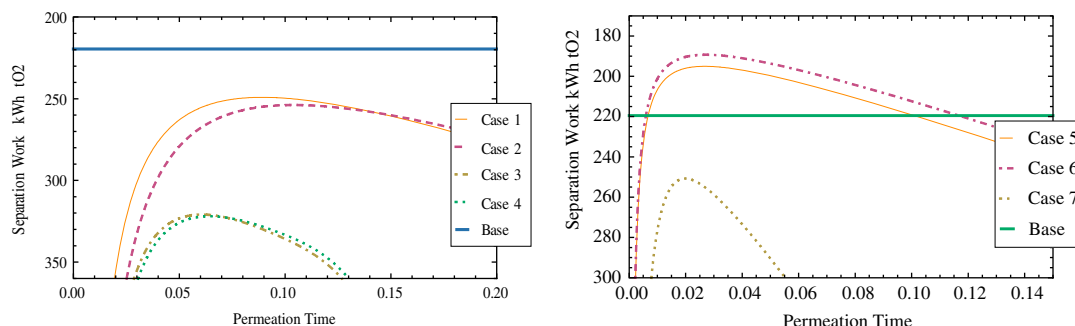


Fig. 18. Separation Work for Cases 1–4 (left) and Cases 5–7 (right) in Large Production Scale (1000's tn/day). Selectivity of 8, Pressure Ratio of 3 and η of 90%.

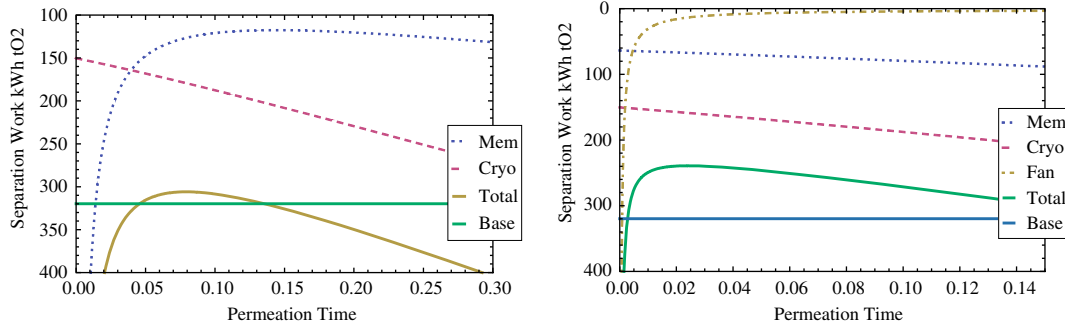


Fig. 19. Separation Work for Case 1 (left) and Case 6 (right) in Small Production Scale (500–1000 tn/day). Selectivity of 8, Pressure Ratio of 3 and η of 90%.

entire arrangement to require less work than the benchmark of 220 kWh/t_n O₂. Although raising the temperature by 40 K is not enough to match the current standard, it gives a substantial reduction in the overall work. Thus, if any excess heat is available in the system, it should be utilized to heat the turbine inlet gas.

5.2. Integration of hybrid design into the oxy-fuel process

The hybrid air separation unit involves both cryogenic and membrane technologies which have to be integrated into an existing or new power plant in order for the plant to operate with sequestration. The overall plant set-up with the hybrid separation unit however is identical to those previously presented for a power plant with oxy-fuel combustion [25]. The only modification involves the air separation unit which would now consist of both the cryogenic and membrane technologies.

Integration of the cryogenic unit has been previously investigated for a variety of cases including advanced supercritical pulverized fuel and natural gas combined cycles [25–28]. Both plants require the high purity oxygen to be mixed with the recycled flue gases to control the adiabatic flame temperature. In view of the fact that the outputs of both a standard cryogenic unit and the hybrid unit are pure oxygen, the integration of oxygen flow to a combined cycle plant would be identical to those previously researched. For the hybrid unit however, the majority of the equipment for the cryogenic component would be smaller as less than half of the gas is required in the input to produce the same output. This is further discussed within the recommendations section of the report.

Integration of the membrane unit could provide challenges due to large scale implementation of the technology. Though it has been suggested that high selectivity O₂/N₂ polymer membranes have the potential to be mass-produced for larger commercial applications [16] [19], no current demonstrations have been made. This production is essential as the membrane area needed for a typical power plant is very large in comparison to the current membrane

applications. From an overall process perspective however the membrane unit is simple; the inlet is ambient air taken from the environment, the outlet is enriched oxygen fed to the cryogenic unit and the waste gas, consisting primarily of nitrogen, is expanded and released back to the environment. If the compressor-turbine arrangement is utilized instead of the vacuum arrangement, any excess heat from the flue gases could be used to increase the work recovered from the turbine. The impact of heating the waste gas can be seen in Fig. 16.

As mentioned in the large scale results section, the hybrid system could increase the efficiency for the entire oxy-fuel plant by 0.9% based upon the chosen parameters. This efficiency could be further increased through advancements in either polymeric membrane or cryogenic technology. To fully realize the benefits and shortcomings of the hybrid design on the oxy-fuel process however, studies such as those by Liszka and Ziebig [29] and use of simulation software such as Aspen Plus® are required. This would give insight into further optimisation possibilities with more control over variable parameters such as pressures, temperatures, equipment efficiencies and mass flows. The current cryogenic model of two compressors could also be enhanced potentially leading to further work reductions.

5.3. Comparison technology

Another membrane technology which has made significant progress toward the mass production of oxygen is the oxygen transport membrane. This ceramic membrane operates at high temperatures upward of 900 °C and transfers oxygen through the membrane wall by a difference in partial pressure that is 100% oxygen selective [30]. The general process is similar to that of the compressor-turbine membrane stage in Fig. 6 except purities of close to 100% are achievable.

Pfaff and Kather [26] show that ceramic membranes can produce oxygen using 585 kWh/t_n O₂ of thermal energy and

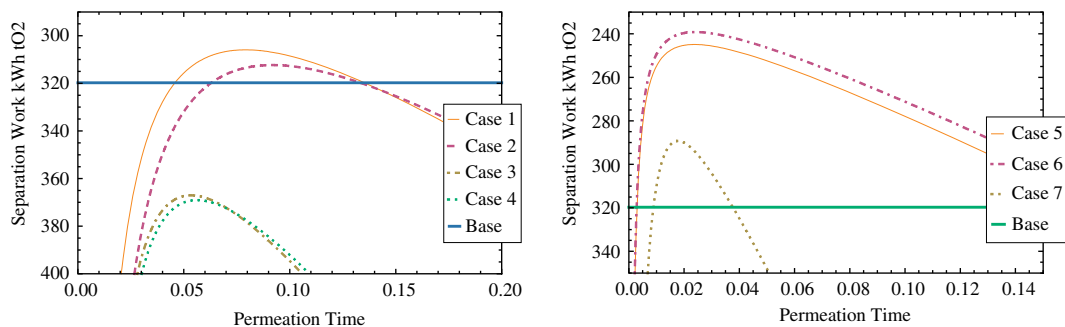


Fig. 20. Separation Work for Cases 1–4 (left) and Cases 5–7 (right) in Small Production Scale (500–1000 tn/day). Selectivity of 8, Pressure Ratio of 3 and η of 90%.

20 kWh/tn O₂ of electrical energy for a given scenario. In the oxy-fuel process most of this energy comes from the combustion flue gases which make it difficult to compare directly to the 190 kWh/tn O₂ of electrical energy found to be required by Case 6. When the potential of the ceramic membrane for oxygen supply to the oxy-fuel plant is compared to that of cryogenic distillation however, no appreciable efficiency benefit was found for the hard coal fired reference plant. It should be noted that Praxair's ceramic membrane oxy-fuel process predicts a 4.6% improvement in HHV efficiency over cryogenic oxy-fuel pulverized coal combustion, though this claim is based upon preliminary findings [31].

The membrane operating temperature is also a point of comparison between technologies. The polymeric membranes for the hybrid process operate at near ambient temperatures preventing any requirement of pre-heating or cooling of the inlet gas [1]. Ceramic membranes however operate at temperatures greater than 900 °C but are able to produce pure oxygen without additional separation.

From a preliminary analysis the ceramic membrane technology would require a much higher degree of integration to the oxy-fuel process than the hybrid system. This is primarily due to the large thermal requirement for the membranes to operate at high temperatures. The ceramic technology is however much further advanced in terms of academic research and implementation. One of the major problems to be overcome is the large energy penalty associated with heating the air to 900 °C for the membrane to operate. Some of the energy can be recovered from the waste gases but the process efficiency suffers. Another issue is the current instability of the membrane material with CO₂ [30].

6. Recommendations

Based upon the above evaluation several recommendations can be made regarding a hybrid air separation unit.

As briefly discussed by Baker [10], the compressor-turbine arrangements require a large amount of work to separate air into its constituents, which makes it inferior to the current system in use. However, in a power plant environment where waste heat can be taken to heat the waste gas before the turbine, a hybrid system may become worthwhile. Additionally, as membrane materials are improved, selectivities will increase, allowing for this arrangement to become a more viable option.

The systems tested in this article focused on oxygen production for use in the oxy-fuel process, which requires large oxygen production of several thousand tons of oxygen per day. However, the hybrid system may be better suited for small to medium applications to replace cryogenic systems that produce oxygen in the order of one hundred tons/day. One problem for large scale production is the surface area of membranes that would be required to produce such a large quantity of oxygen. On the other hand, smaller cryogenic systems are more inefficient than larger ones due to energy loss associated with smaller volumes of air. The hybrid system would benefit from this; while the work from the cryogenic stage depends on the size of the operation, the membrane work would stay the same as it operates closer to ambient conditions. Again, from the results presented above, the recommended design is a vacuum pump system (Case 6).

Several benefits of using a hybrid system, regardless of the scale of the operation, include the possibility of downsizing the cryogenic system by up to 50% depending on the concentration of oxygen in the enriched air. Other opportunities may exist in a redesign of the cryogenic stage. While some current designs require two distillation columns to produce high purity oxygen, the possibility exists to limit this to one column if the purity of oxygen entering the cryogenic system is high enough. Optimization of the

cryogenic stage with oxygen enriched air could lead to further reductions in work for the hybrid system, allowing for it to become a more viable alternative. The detailed discussion of this is beyond the scope of this paper, but further investigations are warranted as they may reduce the overall cost for oxygen production.

The thermodynamic model used in the above analysis is based upon several assumptions. A primary assumption is that no pressure is lost on the feed side of the membrane. In actuality the pressure will decrease slightly from friction and permeation of the gas. Though this loss would be small overall, it is not accounted for in the analysis. The membrane is also assumed to be adiabatic. This implies for the compressor-turbine arrangements that the outlet temperature of the compressor is the inlet temperature of the turbine. Through heat loss in the membrane stage some heat would be transferred to the ambient surroundings, decreasing the waste gas temperature, which would effectively reduce the work output of the turbine. Another part of the model which should be looked at in greater detail is the cryogenic stage. Although the two-stage compression represents a major part of the cryogenic work, a full analysis should be done on an industrial process to determine the full effects that a hybrid process would have.

Another major assumption is that the gas on the feed side is thoroughly mixed. This means that at all times along the membrane a cross-sectional volume of gas has the same composition. If the gases are not thoroughly mixed, oxygen depleted gas could be stagnant along the membrane while gas higher in oxygen concentration would flow through the feed side without passing through the membrane. This would result in a larger amount of compressor work as more gas would have to be processed to obtain the same amount of product.

7. Conclusions

Thermodynamic models were used to test the possibility of reducing the work required to produce high purity oxygen using a hybrid membrane and cryogenic system. Several permutations were evaluated including a compressor-turbine, vacuum pump, two-stage compression and two-stage membrane systems. The compressor-turbine arrangements were deemed unsuccessful without heat addition while the vacuum pump configuration was an improvement of the current system pending a minimum selectivity of approximately four. Both ideas have merit in certain applications, most notably small to medium scale production. The effect of the hybrid design on the oxy-fuel process was also analyzed and found to improve the process efficiency by 0.9%.

This method can also be used to decrease the size of the cryogenic equipment. If only half of the volume of (enriched) air needs to be processed due to a higher oxygen concentration, compressors, piping and distillation columns can all be reduced in size. Further optimization possibilities exist for a cryogenic system which utilizes oxygen enriched gas instead of air. This includes reducing the number of distillation columns and a potential decrease in initial compression pressure.

The overall benefit of a hybrid system is that improvement to either membrane or cryogenic technologies will improve the hybrid system as well. With the numerous oxygen production plants existing around the world, and the potential for even more with the oxy-fuel process, any reduction in work requirements will benefit the industry substantially.

Acknowledgements

Support in the form of an Undergraduate Student Research Award (USRA) by the Natural Sciences and Engineering Research Council (NSERC) is greatly appreciated. The authors also

acknowledge the unwavering support of colleagues and friends whose stimulating conversations allowed this paper to come to fruition.

Appendix A

A.1. Derivation of Eq. (8)

Calculation of the initial oxygen concentration of the permeate stream is non-trivial as the initial amount of each component on the permeate side is equal to zero. As seen from Eq. (6), substitution of the initial amount of moles would then result in a division by zero. It is then necessary to evaluate the initial mole concentration at an infinitesimal time Δt as this time approaches zero. Using Eq. (6), the mathematical argument is as follows

$$X_{1p}(\tau = 0) = \lim_{\Delta t \rightarrow 0} X_{1p}(\Delta t) = \lim_{\Delta t \rightarrow 0} \frac{n_{1p}(\Delta t)}{n_{1p}(\Delta t) + n_{2p}(\Delta t)} \quad (25)$$

Since the initial mole amounts on the permeate side are equal to zero, $n_{1p}(\tau = 0) = n_{2p}(0) = 0$, Eq. (25) can be written as

$$X_{1p}(\tau = 0) = \lim_{\Delta t \rightarrow 0} \frac{[n_{1p}(\Delta t) - n_{1p}(0)]}{[n_{1p}(\Delta t) - n_{1p}(0)] + [n_{2p}(\Delta t) - n_{2p}(0)]} \quad (26)$$

By multiplying the numerator and denominator by $1/\Delta t$ and evaluating the limit, Eq. (8) can be achieved

$$\begin{aligned} X_{1p}(\tau = 0) &= \lim_{\Delta t \rightarrow 0} \frac{\frac{[n_{1p}(\Delta t) - n_{1p}(0)]}{\Delta t}}{\frac{[n_{1p}(\Delta t) - n_{1p}(0)]}{\Delta t} + \frac{[n_{2p}(\Delta t) - n_{2p}(0)]}{\Delta t}} \\ &= \frac{\frac{dn_{1p}}{d\tau}}{\frac{dn_{2p}}{d\tau} + \frac{dn_{1p}}{d\tau}} \quad (27) \end{aligned}$$

References

- [1] Smith AR, Klosek J. A review of air separation technologies and their integration with energy conversion processes. *Fuel Processing Technology* 2001;70:115–34.
- [2] Meyer RE, Heleen de LC. Carbon dioxide capture and storage technical summary. IPCC Working Group III Special Report 2005 p. 24–9.
- [3] Jericha H, Gottlich E, Sanz W, Heitmeir F. Design optimization of the Graz cycle prototype plant. *ASME J Eng Gas Turbines Power* 2004;126:733–40.
- [4] Marin O, Bourhis Y, Perrin N, Zanno PD, Viteri F, Anderson R. High efficiency, zero emission power generation based on a high temperature steam cycle. In: 28th International technical conference on coal utilization & fuel systems. Clearwater, FL, USA, 2003 p. 1–6.
- [5] Zhang N, Lior N. Two novel oxy-fuel power cycles integrated with natural gas reforming and CO₂ capture. *Energy* 2008;33:340–51.
- [6] Ishida M, Jin H. A new advanced power-generation system using chemical-looping combustion. *Energy* 1994;19:415–22.
- [7] Kvamsdal HM, Jordal K, Bolland O. A quantitative comparison of gas turbine cycles with CO₂ capture. *Energy* 2007;32:10–24.
- [8] Koros WJ, Mahajan R. Pushing the limits on possibilities for large scale gas separation: which strategies? *J Membr Sci* 2000;175:181–96.
- [9] Anheden M, Yan J, De Smedt G. Denitrogenation (or Oxyfuel Concepts). *Oil & Gas Science and Technology* 2005;60:485–95
- [10] Baker R. Future directions of membrane gas-separation technology. *Ind Eng Chem Res* 2002;41:1393–411.
- [11] Agrawal R, Auvil SR, Choe JS, Woodward DW. Membrane/cryogenic hybrid scheme for argon production from air. *Gas Separat Purif* 1990;4:75–80.
- [12] Jeon SK, Park YK, Kim JK, Dong JI, Kim S, Kim JM, et al. Membrane/PSA hybrid process for carbon dioxide recovery at low concentration. *Studies in Surface Science and Catalysis* 2004;153:543–6.
- [13] Pandey P, Chauhan RS. Membranes for gas separation. *Prog Polym Sci* 2001;26:853–93.
- [14] Lababidi HMS. Air separation by polysulfone hollow fibre membrane permeators in series. *Trans IChemE* 2000;78:1066–76.
- [15] Cengel Y, Boles M. *Thermodynamics: an engineering approach*. 5th ed. New York: McGraw-Hill; 2006.
- [16] Bisio G, Bosio A, Rubatto G. Thermodynamics applied to oxygen enrichment of combustion air. *Energy Conversion and Management* 2002;43:2589–600.
- [17] Robeson LM, Burgoyne WF, Langsam M, Savoca AC, Tien CF. High performance polymers for membrane separation. *Polymer* 1994;35:4970–8.
- [18] Robeson LM. The upper bound revisited. *J Membr Sci* 2008;320:390–400.
- [19] Seo Y, Kim S, Hong SU. Highly selective polymeric membranes for gas separation. *Polymer* 2006;47:4501–4.
- [20] Allen JB. Making oxygen on the moon. *Popular Sci* 1995;23.
- [21] Seltzer A, Fan Z, Hack H. Oxyfuel coal combustion power plant system optimization. Foster Wheeler North America Corporation R&D; 2007. pp. 1–17.
- [22] Hong J, Chaudhry G, Brisson JG, Field R, Gazzino M, Ghoniem AF. Analysis of oxy-fuel combustion power cycle utilizing a pressurized coal combustor. *Energy* 2009;34:1332–40.
- [23] Kauranen P. Oxygen carriers for power efficiency. VTT Technical Research Facility of Finland; 2008. pp. 1–3.
- [24] Davison J. Performance and costs of power plants with capture and storage of CO₂. *Energy* 2007;32:1163–76.
- [25] Buhre BJP, Elliot LK, Sheng CD, Gupta RP, Wall TF. Oxy-fuel combustion technology for coal-fired power generation. *Progress in Energy and Combustion Science* 2005;31:283–307.
- [26] Pfaff I, Kather A. Comparative thermodynamic analysis and integration issues of CCS steam power plants based on oxy-combustion with cryogenic or membrane based air separation. In: Proceedings of the 9th International Conference on Greenhouse gas control Technologies-GHGT-9 2008. Washington DC, USA: Energy Procedia; 2009. p. 495–502 (1).
- [27] Dillon DJ, Panesar RS, Wall RA, Allam RJ, White V, Gibbins J, Haines MR. Oxy-Combustion Processes for CO₂ Capture from Advanced Supercritical PF and NGCC Power Plant. In: Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies-GHGT-7 2004, Vancouver BC Canada.
- [28] Wall T. Combustion processes for carbon capture. *Proceedings of the Combustion Institute* 2007;31:31–47.
- [29] Liszka M, Ziebiak A. Coal-fired oxy-fuel power unit-Process and system analysis. *Energy* 2010;35:943–51.
- [30] Leo A, Liu S, Diniz da Costa JC. Development of mixed conducting membranes for clean coal energy delivery. *International Journal of Greenhouse Gas Control* 2009;3:357–67.
- [31] van Hassel BA, Li J, Wilson J, Degenstein N, Shah M, Christie M, et al. Oxygen transport membrane based oxy-combustion for CO₂ capture from coal power plants. Praxair Technology Inc; 2008:1–17.