Carbon membranes for oxygen enriched air –Part II: Techno-economic analysis

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Highlights:

- Oxygen-enriched air at a concentration of 78 mole % O_2 with carbon membrane
- A single stage process can obtain 99.50% N_2 purity with 75% recovery
- Feed compression and/or permeate vacuum approaches were investigated
- Optimization of the process to produce economical oxygen-enriched air

Abstract

Carbon membrane (CM) separation process for producing oxygen-enriched air (OEA) at a concentration of 50 to 78 mole% O_2 in a single stage process with no recycle stream has been investigated. This paper (Part II of a two-part study) considers techno-economic analysis for O_2-selective carbon membranes to yield the lowest production cost of "equivalent" pure oxygen (EPO_2) in a single stage separation process based on experimental and predictive membrane performance. Aspen Hysys® interfaced with ChemBrane (in-house developed model) was used to perform the simulations for air separation with CM. Three different approaches with respect to pressure were investigated; (1) feed compression, (2) vacuum on permeate side and (3) combination of (1) and (2). The simulation results and sensitivity analysis showed that with current performance (O_2 permeability: 10 Barrer *(1 Barrer =2.736E−09 m^3(STP)m/(m^2 bar h))* and O_2/N_2 selectivity: 18), mechanical properties, and cost per m^2 of CM, it is economically most efficient to use the third approach "combination of feed compression and permeate vacuum" to produce EPO_2. A stage cut of 10% was found to be as an average economical optimum when using vacuum pump (approach (2)) to produce OEA.

However, the techno-economic analysis for the reported CM showed that a stage cut of 0.15-0.2 was the most cost-effective while using compression approach (1) or (3) to produce EPO_2.

Key words: Oxygen enriched air, carbon membrane, simulations, Techno-economic analysis

1. Introduction

Cryogenic distillation is the most common technology to produce high purity oxygen (>99%) at large scale productions (100-300 tons/day). Pressure swing adsorption (PSA) can reach up to 95% oxygen purity and the requirement of sorbents limits the size capacity for small to medium scale plant (20-100 tons/day), mainly due to high capital cost. However, both cryogenic and PSA are considered as energy intensive technologies [1, 2]. Therefore, energy efficient methods with low capital investment are required to separate the air into oxygen (as enriched air or pure oxygen) and nitrogen.

Membrane separation is an attractive process alternative due to its simple design, lower energy demand, smaller footprint, good weight efficiency (light weight equipment compared to other technologies), and flexible, modular design. However, compared to conventional technologies commercially available polymeric membranes can not economically produce high purity of O_2. The performance of polymeric membranes is restricted by the trade-off between permeability and selectivity [3]. Polymeric materials may have high permeability for O_2, but rather low O_2/N_2 selectivity (usual range 2-8), and the maximum permeate purity achievable for O_2 with polymeric membranes seems to be 30-60% [4]. Nitrogen of purity up to 99.5% can be produced using polyimide membranes (O_2/N_2 selectivity of 9) [3, 5]. Nevertheless, a multi stage separation process with recycle stream is required to achieve high recovery of N_2 which would add more cost and complexity to the system.

High purity oxygen is difficult using membranes because of the high content of nitrogen in the air, (79%) and the relative low selectivity of O_2/N_2 resulting in oxygen enriched air (OEA) in permeate, rather than pure oxygen. Based on the performance of commercially available polymeric membranes, the separation process is competitive only for medium O_2 purity (25-40%) and small-scale plants (10-25 tons/day) [4, 6]. OEA is already used for numerous chemical processes (Claus process, the Fluid Catalytic Cracking technology, the oxidation of *p*-xylene to give terephthalic acid) combustion processes (natural gas furnaces, coal gasification), medical purposes, and has more recently also attracted attention for hybrid carbon capture process [7].

Carbon is a class of material that can offer improved performance due to molecular sieving effect. In molecular sieving, the available pore size is below the kinetic diameter of one of the gas components in the feed. This characteristic of the material increases selectivity by reducing the rotational degrees of freedom of nitrogen versus oxygen in the diffusion (kinetic) transition state. In addition, carbon membranes (CM) offer superior thermal resistance and chemical stability in corrosive environments [8]. Many prior studies have reported higher selectivity and permeability of CM compared to polymeric membranes for air separation [9-13].

In 1991, Bhide and Stern calculated the membrane performance required to produce OEA at a cost competitive to cryogenically produced oxygen at $40-60/ton of equivalent pure oxygen (EPO_2) [4]. They showed that none of the today's polymers can reach the $40-60/ton EPO_2 target. To reduce the capital and production cost (PC) of the membrane-based process, both selectivity and permeability must be improved. Higher O_2/N_2 selectivity is required to reach the high purity of O_2 with a lower driving force (partial pressure ratio) hence, the operating cost will be reduced. A higher permeability of O_2 will cut the required membrane area for the separation, therefore, low capital investment is needed. Much academic research is focused on producing highly selective membranes, but if the membranes then have too low permeabilities they are most likely not an optimum choice for the application in focus. The carbon membranes reported here were experimentally documented to have a high selectivity 18 for O_2/N_2 and the permeability of O_2 was increasing exponentially with increase in operating temperature without significant loss in the selectivity [14]. Hence it was found that the separation process with these carbon membranes may be optimized to achieve high purity O_2 with reasonable capital investment and production cost. Predicting the cost of carbon membrane modules is difficult because of the lack of commercial precedent. Based on pilot scale production cost of regenerated cellulose-based CM, this paper focuses on the techno-economical analysis of CM-based air separation process to investigate the viability of CM in OEA market.

In order to obtain OEA economically with polymeric membranes, feed compression is not considered a viable solution due to the high energy cost. Some studies have concluded that applying vacuum on permeate side corresponds to the lowest energy requirement whatever the membrane stage cut is ($\theta = q_p/q_f$, defined as the ratio of permeate flow rate to feed flow rate), because only the permeate stream has to be processed which is a small portion of the feed [4, 7]. However, in this study we will compare the three compression approaches; feed compression, permeate vacuum, and a combination of both feed compression and permeate vacuum. The simulation results and sensitivity analysis show that with the present

performance, mechanical properties, and cost per m^2 of CM, it is more economical to use a combination of feed compression and permeate vacuum for small scale OEA production.

This study is comprised of two parts. Part I of this study [14] describes laboratory testing of carbon membranes for air separation and regeneration techniques (thermal, chemical and electrical) to achieve a stable performance of the membrane. The CM was shown to exhibit single gas O_2/N_2 selectivity of 18 and O_2 permeability of 10 Barrer *(1 Barrer =2.736E−09 m^3(STP)m/(m^2 bar h))* at 68 °C. The permeability of O_2 was increasing exponentially with increase in operating temperature without significant loss in the selectivity. Part II of this study (discussed here) examines the economic viability of carbon membranes in the air separation market. Aspen Hysys® interfaced with Chembrane, an in-house built membrane model was used for the simulations. Single stage configuration with CMS membrane was optimized to attain a simple process with minimum cost to produce OEA. The separation properties of the prepared CM were predicted to achieve high O_2 permeability, between100-300 Barrer, by keeping the selectivity constant. It has been documented that the assumption on the higher O_2 permeability without sacrificing the O_2/N_2 selectivity, may be achieved by adding the nano particles in the precursor [15, 16] or operating the membranes at elevated temperature. The separation process was optimized with respect to installed energy and membrane area to achieve low production cost and total capital investment (TCI). The sensitivity of the process towards membrane area, energy, membrane life time, and membrane cost was investigated in the current study.

Simulation results indicated that these membranes may produce 78% O_2-enriched permeate stream and at the same time obtain 15% O_2 (hypoxic) retentate stream in a single-stage process when using combination of feed compression and vacuum on permeate side. Although retentate stream usage is not considered in the economic calculations, the retentate stream may be used as hypoxic air (Air containing 15 vol.% O_2 is named as hypoxic air, and over the last years use of the hypoxic air has increased in venting system to reduce the fire hazards. Further, in multifunctional buildings, electrical appliance rooms and computer rooms use of hypoxic air have been found to be essential to societal important functions [17].

2. Background on membrane model and process simulations

Chembrane, an in-housed membrane model, based on mass transfer equations for co-current, counter current, and a perfectly-mixed flow configuration, was interfaced with Aspen Hysys® V9. The thermodynamic fluid package that uses sour Peng-Robinson equation of state was used

to perform all the simulations for air separation with CM. For a shell fed module, based on MemfoACT AS module design [18], the counter-current configuration explains real behavior of gas flow as the best. Therefore, counter-current configuration was also used in the current study. However, other configurations and details of the model can be found elsewhere [19].
A representation of membrane module counter-current configuration is shown in figure 1.

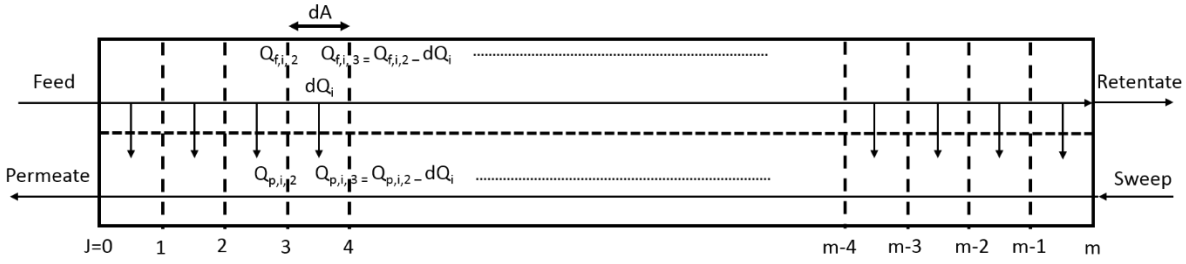


Figure 1: Counter-current gas flow configuration through a membrane [19]

The membrane was divided into m equal area, perfectly mixed stages. Assuming a dense, symmetric membrane, the mole flux for each component, i, on the feed side is given by:

$$dQ_{f,i} = P_i.\left(P_f.x_{i,f} - P_p.y_{i,p}\right).dA \qquad (1)$$

where $Q_{f,i}$ is the molar flow of i in the feed, P_i is the permeance for i, P_f is the feed side pressure, P_p is the permeate pressure, $x_{i,f}$ is the molar fraction of i in the feed side increment, $y_{i,p}$ is the molar fraction of i in the permeate side increment and A is the membrane area.
The counter-current configuration is complicated to solve, because a concentration profile exists on the permeate side and the permeate exit flows at j=0 are unknown. An initial estimate for the concentration profile is needed to solve the set of non-linear differential equations. Since the permeate and feed flows are in opposite directions, equation (2) may be stated:

$$dQ_{f,i,j} = dQ_{p,i,j} \qquad (2)$$

Instead of requiring an initial estimate of the steady state concentration profile, this model solves a total permeate pressure of zero in the first iteration, for which the solution of the mole balance equation (1) is insignificant (the value of the second term in parentheses is zero). The permeate pressure is then increased by an increment. The concentration profile generated in the first iteration is used to solve the system in the second iteration. In this manner, the permeate

pressure is increased until the actual (steady state) permeate pressure is reached, with small enough increments that the concentration profiles change slightly with each increment. The method is analogous to starting up a membrane module with full vacuum on the permeate side and allowing the pressure to rise by throttling the outflow of permeate. The model uses fourth-order Runge-Kutta method to calculate the flux along membrane length and then uses iterations over permeate values to converge to a solution.

3. **Simulation basis and economic parameters**

3.1. Experimental data

In this section, gas separation properties of CM, obtained through experiments (Part I [14]), were used to simulate the optimal conditions for production of OEA. The permeability and selectivity data for carbon membranes are experimental data obtained at different temperatures, 5 bar feed pressure and vacuum (10 mbar) on low pressure side, are listed in table 1.

The driving force is the difference in partial pressures of the components on both sides of the membrane, and this difference is achieved in the simulations by compressing the feed and/or reducing the permeate pressure. The ratio between feed side pressure and permeate side pressure ($\Psi = P_{permeate} / P_{feed}$) is a key operating parameter that effects both separation performance and energy requirement [20].

To achieve required pressure ratio in the simulations, three different compression approaches as shown in figure 2 (a), (b), (c) were used to obtain the required energy and membrane area:

- *Feed compression (FC)*; a feed compressor was used to compress the air to 10 bar.
- *Vacuum pump on permeate side (VP);* No compression of the feed air, a vacuum pump was used to create 10 mbar on permeate side of the membrane.
- *Combination of Feed compression and permeate vacuum (FC-VP)*; In this case, feed air was compressed to 10 bar, and vacuum (10 mbar) was used on permeate side of the membrane.

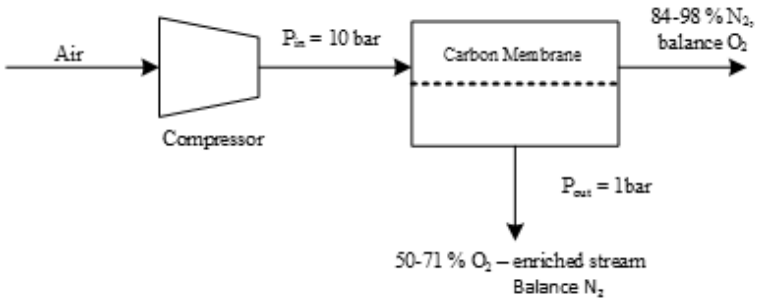
An ideal gas was considered in the simulations. CMs based on molecular sieving for mixed gases like O_2 and N_2 show separation properties which is equal to or better than single gases [21, 22]. Countercurrent gas transport without any sweep on low pressure side was modeled. The membrane process was broken down into 150 discrete stages and the mass balance was determined iteratively for each stage. Process simulations and economical assessment were done for a CM unit which would increase O_2 concentration (based on permeation values) in air

from 21 mole % to between 50-78 mole % in a single stage separation process (no recycle). A single stage membrane system has many advantages; it is simple, compact and passive with no moving parts, except some auxiliary equipments (compressor and vacuum pump). The system is easy to operate when no recycle stream is present. An optimal module design may require only one membrane skid for the whole system and that would significantly reduce the module housing, valves and piping cost. A single stage membrane system is flexible to be linearly scaled up or down, however, scalability of multi stage system with recycle stream is more complex due to involvement of parameters such as inter-stage pressure and recycle ratio.

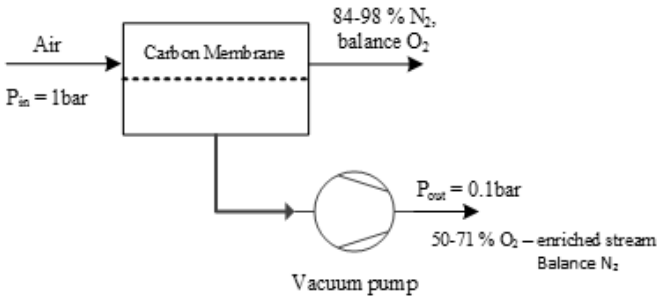
Table 1: Experimental data for simulations

Temperature (°C)	O_2 Permeability (Barrer)	Selectivity O_2/N_2
20	2.98	18
35	4.58	18
45	5.88	19
50	6.41	19
68	9.93	18

(1 Barrer =2.736E−09 m^3(STP)m/(m^2 bar h))



(a)



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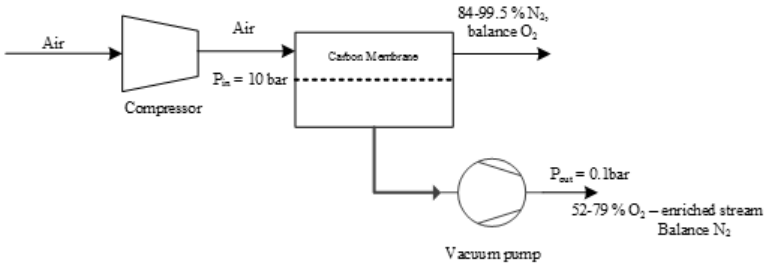

(c)

Figure 2: Single stage process configuration, (a) FC approach, (b) VP approach, (c) FC-VP approach

3.2. Equivalent pure oxygen, EPO_2

The base for the O_2 production was taken to be 1 ton of EPO_2 per day, and EPO_2 is the amount of pure oxygen that would be mixed with air to make a mixture of OEA (n moles) of a specified O_2 concentration. The molar flow rates of EPO_2 and OEA can be related by the simple equation shown as equation 3 [4].

$$\frac{n\ EPO_2}{n\ OEA} = \frac{y_{O_2} - 0.21}{0.79} \qquad (3)$$

Here "n EPO_2" is the molar flow rate (moles/day) of EPO_2 and "n OEA" is the molar flow rate (moles/day) of OEA, y_{O_2} is the oxygen mole fraction in OEA.

In terms of weight, the flow rates (tons/day) of EPO_2 and of OEA are related as shown in equation 4.

$$\frac{TEPO_2}{TOEA} = \frac{y_{O_2} - 0.21}{(0.0989\, y_{O_2} + 0.692)} \qquad (4)$$

Here $TEPO_2$ is the mass flow rate (tons/day) of EPO_2 and TOEA is the mass flow rate (tons/day) of OEA, y_{O_2} is the oxygen mole fraction in OEA.

Figure 3 presents the single stage process simulation diagram in Hysys®. Pressure and feed flow are adjusted to optimize the trade-off between membrane cost and compression duty cost, and finally to yield the lowest production cost of EPO_2. Permeate stream is an O_2-enriched stream (50-78% O_2) with mass flow adjusted for 1 ton per day of EPO_2. Oxygen molar concentration varies in the retentate stream depending on the stage cut, the area used, and feed pressure.

Considering an economically feasible scenario, O_2 concentration ranges from 3% to 15% balanced with N_2 in the retentate gas stream. Although retentate is not considered in the economic calculations, the retentate stream could be used as hypoxic air (15% O_2) or in another case as 97% N_2 stream as blanketing gas to prevent hazardous conditions [17].

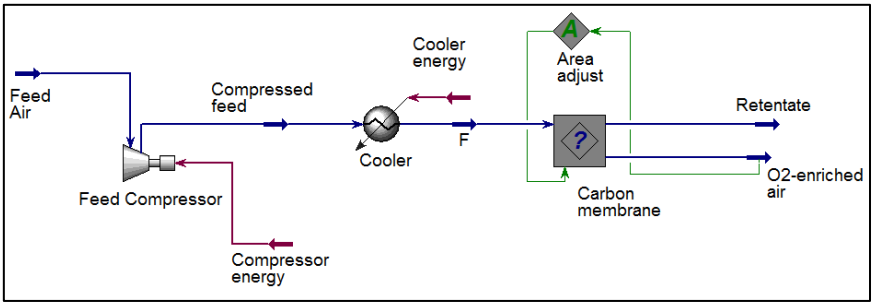

Figure 3: Single stage separation process in Hysys® simulations

3.3. Predicted values of O_2 permeability

CM have superior thermal resistance compared to polymeric membranes and can be operated at elevated temperatures. The reported membranes showed exponential increase in O_2 permeability with increasing temperature and according to Arrhenius model (extrapolation of experimental data as in **table 1**), the separation process at elevated temperature between 190-205 °C using reported CM may achieve high permeability of O_2 without sacrificing the selectivity. Another solution may be to achieve high permeability by adding some nano

particles to the precursor [16]. Liu et al. [15] prepared a carbon/ZSM-5 nanocomposite membrane incorporating different weight% of nano particles (ZSM-5) in the polyimide precursor and carbonizing it at 600 °C. They have reported experimental results at 25 °C which showed an increase in O_2 permeability from 2.21 Barrer prior adding nano particles to 499 Barrer with 16.7 wt% of the nano particles. The O_2/N_2 selectivity loss was only 9%.

Three permeability values; 100, 200, and 300 Barrer with constant O_2/N_2 selectivity of 18 were considered in the current work to investigate the effect on production cost of EPO_2 and total capital investment of the plant. Parameters and operating conditions used in simulations are shown in table 2.

Table 2: Parameters used to simulate the single-stage air separation process

Feed composition	21 vol.% O_2, 79 vol.% N_2
Permeate flow rate	1 ton per day of EPO_2
Permeate composition	50-78 mole% of O_2; balance N_2
Permeate pressure	1 bar (10 mbar in vacuum mode)
Feed flow rate	variable*
Feed pressure	10 bar for FC and FC-VP approach, 1 bar for VP approach
Adiabatic efficiency of compressor and vacuum pump	75%

** Feed flow rate and feed pressure are adjusted to optimize the membrane area and compressor energy consumption*

3.4. Economic parameters

The cost of an installed membrane separation process is determined by two contributions, the capital cost, and the operating cost. In this cost analysis, capital cost includes membrane modules cost, compressor cost, and vacuum pump cost. Whereas, operational cost involves membrane replacement cost during the expected lifetime of the plant, plus the power requirement for compression and vacuum pump and labor cost. The economic evaluation of a given membrane separation process can significantly vary depending on the method used for

analysis, the cost of raw materials, equipment and utility cost, labor cost, depreciation policy, interest rates etc.

The assumptions and parameters used in the present economic assessment are shown in table 3. CM module cost is considered \$100 per m^2 based on pilot scale manufacturing of CM [23]. Predicting the cost of CM modules and life of the membranes is challenging due to the lack of commercial precedent. The expected life of the membrane is considered as 5 years. However, based on pilot scale demonstration of CM at biogas plant [24], it was observed that some of the CM modules may experience fiber breakage (due to vibration or handling / shipping of the modules) and therefore, cannot be used until repaired. Again, other modules may perform well for longer time. The first-time installation of membrane modules was included in the TCI. However, membrane replacement cost (MRC) was added in PC as a variable cost which is proportional to plant's operation rate. MRC was calculated based on daily usage (1 ton/day production of EPO_2) via dividing the total membrane area cost by total plant life (10 years) and then multiplied by plant availability (90%). MRC, electricity cost, capital recovery cost, and total labor costs were added to get PC of EPO_2.

The techno-economic calculation is based on a small-scale plant (1 ton/day). The membrane operation does not need continuous labor. Therefore, labor cost (LC) has been estimated as 8 hr/day per 25 tons per day of EPO_2. The total labor was twice the labor cost which includes: maintenance (5% of LC), supervision (15% of LC), benefits (40 % of LC), and plant overheads (40% of LC). This cost analysis considers a CM price of \$ 100/m^2, a depreciation rate of 10% for the plant which includes compressor, vacuum pump, valves, and piping (except membrane), and a return on investment of 12%/year.

Table 3: Economic parameters used to calculate TCI and PC per ton of EPO_2 [4, 25]

Total capital investment (TCI)	
CM module cost: CMC	$\$100/m^2$
Installed compressor cost: CC	$\$ 8,700 \times ([a]HP)^{0.82}$
Installed vacuum pump cost: VC	$\$32,500 \times ([a]HP/10)^{0.5}$
Production cost (PC)	
Membrane replacement cost: MRC	at $\$100/m^2$
Electricity cost: EC	\$0.05/kWh
Capital recovery cost: CRC	0.25 x (TCI)
Labor cost: LC	\$15/hr
Production cost: PC	MRC + EC + CRC + TLC
Other assumptions	
Membrane life time	5 years
Annual depreciation of the plant except membrane	10% over 10 years
Annual Return on capital investment	12%
Plant availability	90% (329 days/year)
Labor requirement	8 hr/day per 25 tons per day of EPO_2
Total labor cost (TLC)	2 x LC

[a]*HP is the installed horse power for the installed compressor*

The CM offer a high O_2/N_2 selectivity of 18 to obtain O_2 concentration (50-78%) in a single stage process. However, carbon membrane cost is much higher than polymeric membranes. The retentate stream can be adjusted to obtain a required N_2 concentration in a range between 84-99.5%. The assumptions made in this economic analysis involves many adjustable variables, therefore a sensitivity analysis has been performed to determine the cost of EPO_2

which involves variation in CM module cost, membrane life time, and operating temperature which is directly related to membrane permeability.

4. Results and discussions

4.1. Simulations and economic assessment based on experimental data

Figure 4 shows the effect of stage cut (q_p/q_f) on the O_2 concentration in permeate and retentate stream while using different compression approaches. The O_2 concentration would be similar for FC and VP approach due to the same pressure ratio across the membrane in both approaches. However, the concentration values are slightly different for FC-VP approach. The concentration of 78 mole % O_2 at 0.1 stage cut is obtained on the permeate side while using the FC-VP approach. In addition, 15% O_2 was obtained in the retentate stream which is considered as hypoxic air. Although the retentate stream is not considered here in economic calculations, it is still of importance while estimating the full plant cost. At lowest stage cut value, the O_2 concentration in permeate is highest but the flow rate of the permeate is very low because only a small fraction of the feed permeates through the membrane. It can be seen in figure 4 that O_2 concentration is decreasing in both permeate and retentate streams with an increase in stage cut. The stage cut value of 0.4 gives 50 mole % O_2 on the permeate side and almost 99% N_2 in the retentate stream for the membrane with O_2/N_2 selectivity of 18.

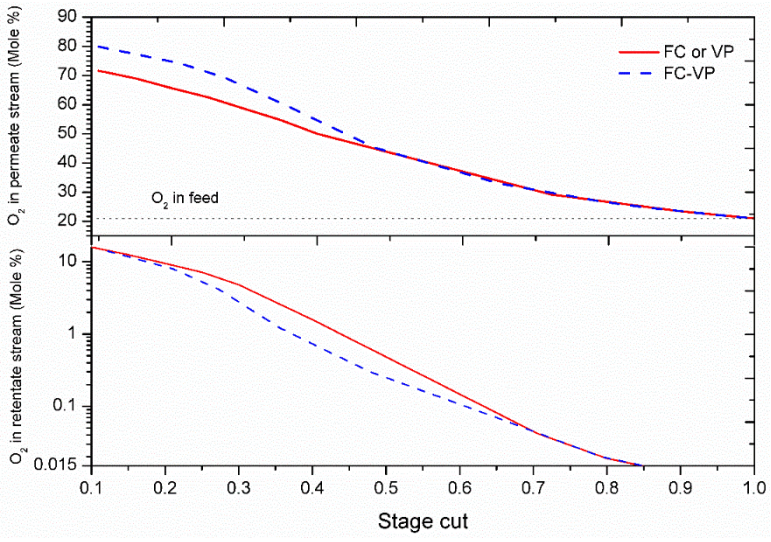

Figure 4: Mole-fraction of O_2 in permeate and retentate streams as function of stage cut in a single stage separation process (O_2/N_2 selectivity: 18)

Figure 5 presents the energy requirement while using different compression approaches. As can be seen FC and FC-VP approaches offer maximum energy requirement at lowest stage cut. However, the energy demand reduces up to 50% at stage cut of 0.25. The FC-VP approach offers high energy requirement because a direct feed gas (air) compression require a higher energy and in this context, using vacuum pump at the same time will need even more power as shown in figure 5. At the contrary, lowest energy requirement of vacuum pumping in VP approach results from the fact that the permeate flow only has to be pumped. The VP approach is an energy efficient process compared to FC, FC-VP, and cryogenic distillation. The membrane area required for a plant to produce one ton of EPO_2 per day is presented in figure 6. As shown in figure 6, the membrane area is minimum at 0.1 stage cut for all three compression approaches. At stage cut of 0.1, the area for the VP approach is 10 times higher than for the FC approach and 15 times larger compared to the FC-VP approach. Here comes the trade-off between membrane cost and energy cost while considering an economically viable process with lowest PC and TCI. Presently, carbon membrane cost is very high, and it is more economical to operate the system at higher pressure instead of using high membrane area which would also result in extra piping, valves, and maintenance cost. In this scenario, VP approach is not viable at even lowest value of membrane area and energy which is at 0.1 stage cut.

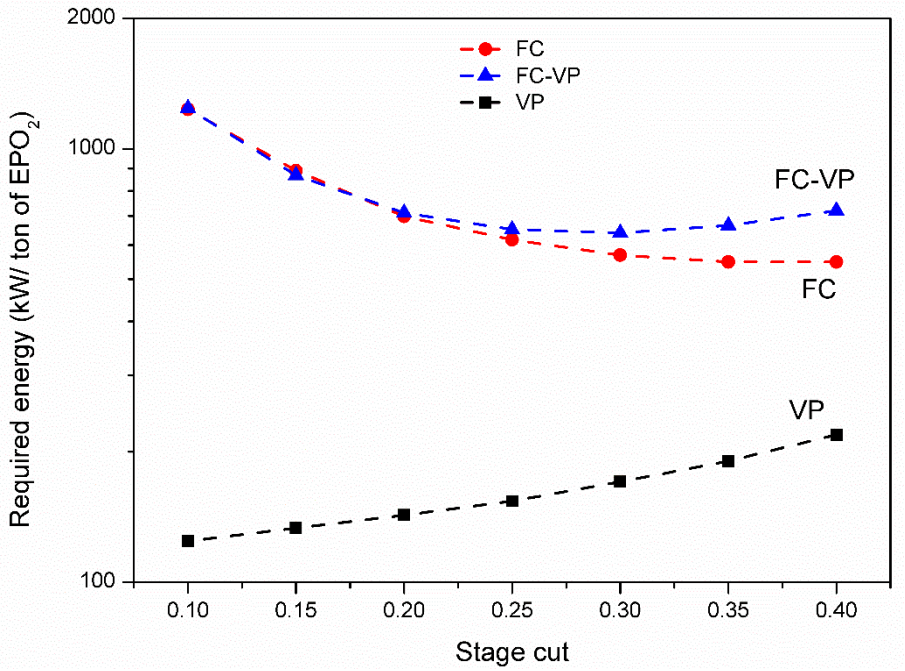

Figure 5: Required energy to produce 1 ton of EPO_2 as a function of stage cut while using different compression approaches (Energy for cryogenic unit: 285 kW/ton of 99.6% O_2 [7])

Figure 6 shows that increasing stage cut value from 0.1 to 0.25 would result in almost 65% rise in required membrane area for all three compression approaches. Due to five years of averaged membrane life-time expectancy, the total membrane area needs to be reinstalled again after five years hence, the cost of membrane is directly related to PC and TCI. On the other hand, the energy cost reduces to half for the FC and FC-VP approaches at stage cut 0.25 and that ultimately would reduce the PC for these approaches. The desired production rate of EPO_2 depends on both the oxygen concentration in the permeate stream and the permeate flow. The trade-off between area and energy is optimized here to get the minimum production cost per ton of EPO_2 at 1 bar in single stage membrane process.

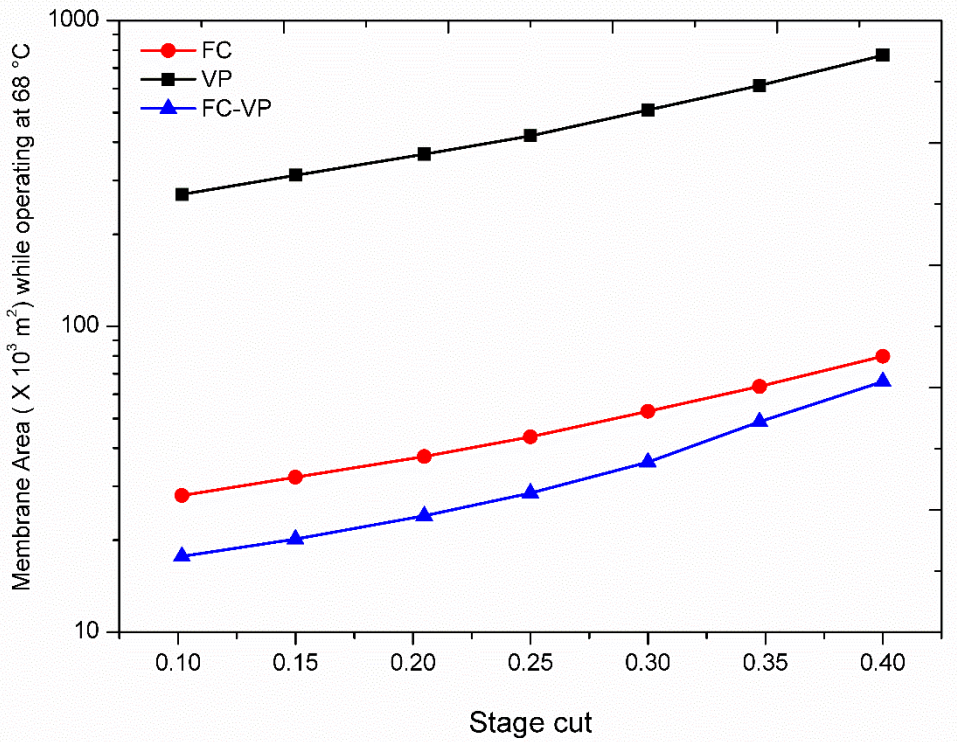

Figure 6: Required membrane area as a function of stage cut while operating at 68 °C (O_2 Permeability: 10 Barrer)

The plots in figure 7 present the production (PC) cost per ton of EPO_2 (bar chart) and total capital investment (TCI) which is shown as scatter plot for a carbon membrane based single stage air separation system at 68 °C. Only the optimal stage cut values with respect to the lowest production cost per ton of EPO_2 for different compression approaches are presented here. All three approaches are optimal at stage cut 0.1 when O_2 permeability is 10 Barrer. The cost per ton of produced EPO_2 and the total capital cost is the minimum for FC-VP approach at 0.1 stage cut. This minimum value is the consequence of lowest membrane area. Due to 5

years of expected membrane life, the one-time replacement would increase the PC to very large value for the VP approach. Higher TCI value results in high capital recovery cost which also adds in PC. The TCI and PC for VP approach are more sensitive to the area than energy due to low permeability at 68 °C.

Although the membrane performance is within the commercially attractive region of Robeson plot as shown in figure 8, and FC-VP approach has lowest production cost $ 644/ton of EPO_2, the price is nevertheless very high compared to other technologies. Increase in O_2 permeability would to some extent would scale down the effect of membrane price on FC-VP approach since the membrane area is optimized for the required production rate.

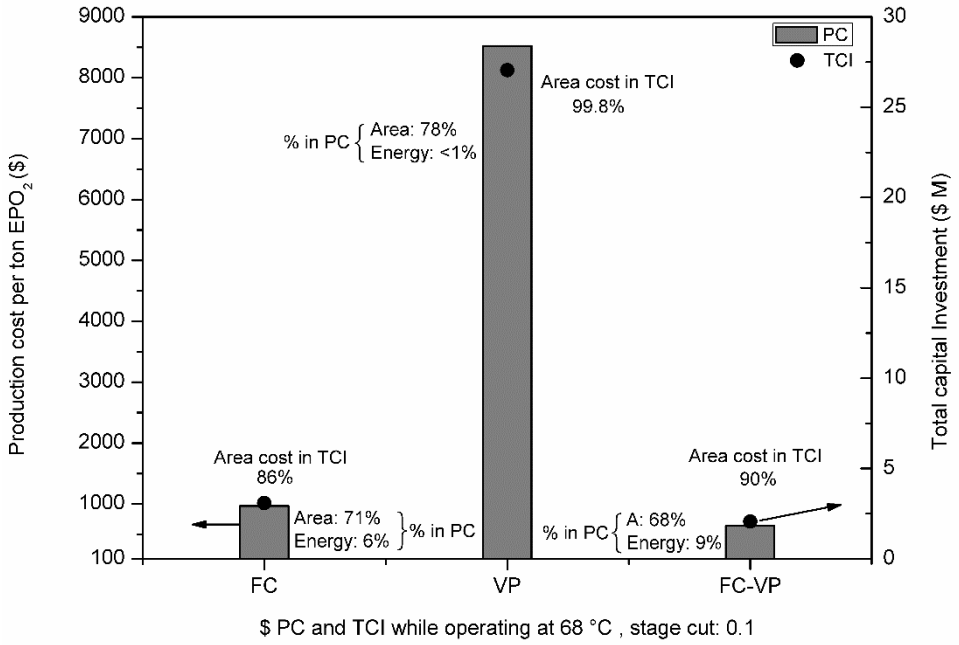

Figure 7: Lowest PC and TCI for different compression approaches at optimal stage cut value (Operating temperature: 68 °C, Permeability: 10 Barrer)

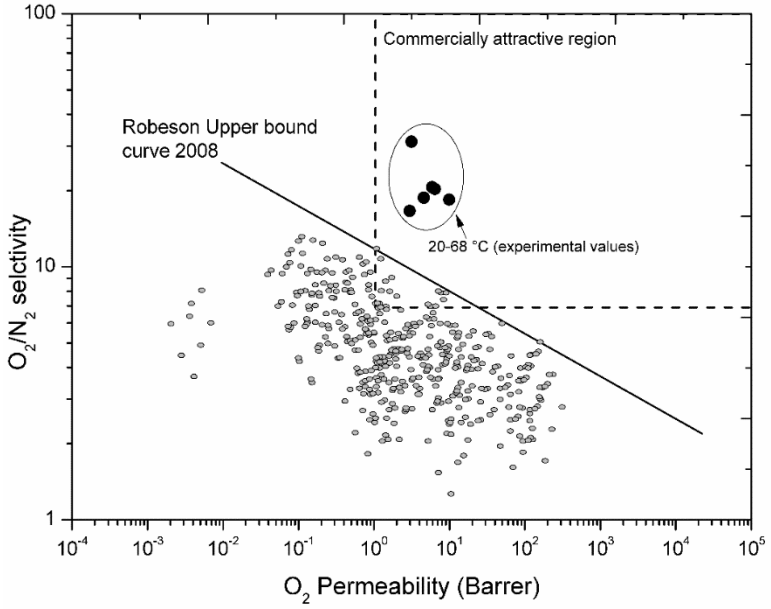

Figure 8: O_2 permeability and O_2/N_2 selectivity of CM with respect to Robeson upper bound curve (2008) [3]

As already shown in table 1, the permeability of O_2 and selectivity of O_2/N_2 are very much dependent on operating temperature. Thus, higher temperature offers high permeability of O_2 with sufficient O_2/N_2 selectivity to keep the membrane in the commercially attractive region as presented in figure 8. Operating membrane at 205 °C gives O_2 permeability of 300 Barrer with O_2/N_2 selectivity of 18 in comparison to operation at 190 °C which offers O_2 permeability of 200 Barrer with O_2/N_2 selectivity of 18 (according to Arrhenius model extrapolation of experimental data shown in table 1). Elevated temperature operations are costly, so the extra energy cost adds up to the TCI and PC per ton of EPO_2. The adiabatic heating of the compressor can be utilized to increase the gas temperature for achieving higher flux. Depending on compressor type, the actual compression may heat the gas significantly to increase the temperature to well beyond 100°C. In addition, the separation operated at elevated temperature may act as regeneration by removing physically adsorbed gases and eliminating the water aging effe on the carbon membranes. However, a good sealing/potting material for module construction is challenging to develop when operating at temperatures higher than 150 °C. Another solution could be to improve O_2 permeability of the membrane without sacrificing O_2/N_2 selectivity; this may be achievable by adding some nano particles to the precursor [15, 16].

4.2. Simulations and economic assessment based on predicted data

Figure 9 is showing the PC and TCI as function of stage cut when O_2 permeability is 100 Barrer and selectivity is 18. The stage cut of 0.1 has been reported as an average economical optimum [4] for VP approach. This study also shows that stage cut of 0.1 is optimal for VP approach however, it is not optimal for FC or FC-VP approaches when O_2 permeability is 100 Barrer as shown in figure 9. The reduced membrane area due to high permeability offers maximum benefit to FC-VP approach in dropping the production cost of EPO_2.

Figure 9 examines the TCI and PC as function of stage cut when EPO_2 is produced using three different compression approaches (O_2 permeability: 100 Barrer, O_2/N_2 selectivity: 18). The lowest production cost \$127 and \$130 are achieved by FC-VP approach at stage cut of 0.17 and 0.20 respectively. Hence, the process is optimal at stage cut of ca. 0.17 for minimum PC and TCI. However, the required membrane area is still very high at stage cut 0.17, and the TCI for the FC-VP approach is almost \$ 0.4 million for a plant to product one ton of EPO_2 per day.

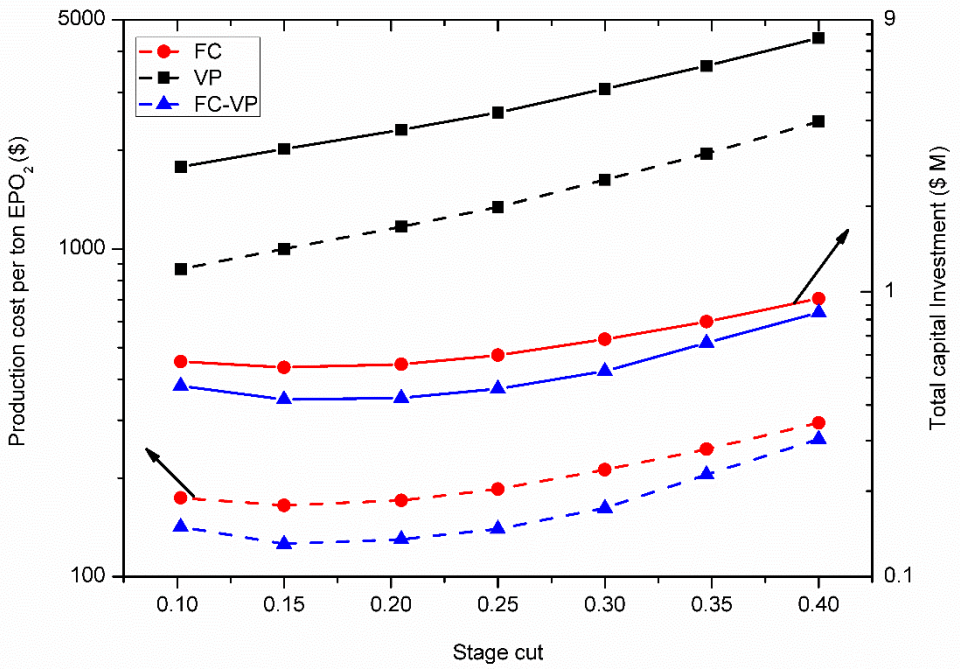

Figure 9: PC and TCI as function of stage cut, O_2 permeability: 100 Barrer, O_2/N_2 selectivity: 18

Figure 10 and 11 show PC per ton of EPO_2 and TCI of the plant while using three different compression approaches when the O_2 permeability is 200 and 300 Barrer respectively. The energy requirement for all cases remains the same due to constant O_2/N_2 selectivity value of 18. When using FC-VP approach, it reduces the membrane area to a large extent and the TCI

and PC are 5 times lower than that of VP approach. As shown in figure 10 and 11, the membrane price had great influence on the capital investment and production cost of EPO_2. Increase in operating temperature or O_2 permeability scale down the effect of membrane area because the required area is being more and more optimized towards the required production rate. Almost similar trend is observed while considering the production cost of EPO_2 using different compression approaches. Although very low energy is required in case of vacuum approach, but membrane life time (5 years in this study) is playing a key role to increase the production cost of EPO_2 in this approach. The membrane cost \$100 per m^2 and reinstallation of total area (9000-270000 m^2 depending on the different cases) keep the PC higher for all operating permeabilities 10-300 Barrer. Nevertheless, the PC is almost hundred dollars for VP approach when O_2 permeability of CM is higher than 1000 Barrer. Hence, VP approach is not a competent choice when O_2 permeability is below 1000 Barrer while the membrane costs \$ 100/m^2, membrane life 5 years, and O_2/N_2 selectivity is 18.

The lowest production cost with CM process is, \$80 /ton of EPO_2 for O_2 permeability of 300 and TCI for the corresponding plant is \$264,000 while using FC-VP approach as shown in figure 11. This production cost is comparable with PSA plant that costs \$100/ton of EPO_2 at a plant capacity of 1 ton per day. Nevertheless, the most economical process of producing O_2 on a large scale is by the cryogenic distillation and the cost can be as low as \$ 25/ton at plant capacities above 100 tons/day of EPO_2 [4]. Hence, the TCI and PC of EPO_2 while operating at elevated temperature of 205 °C or permeability up to 300 may compete with PSA plants for small scale plants (1-10 tons/day).

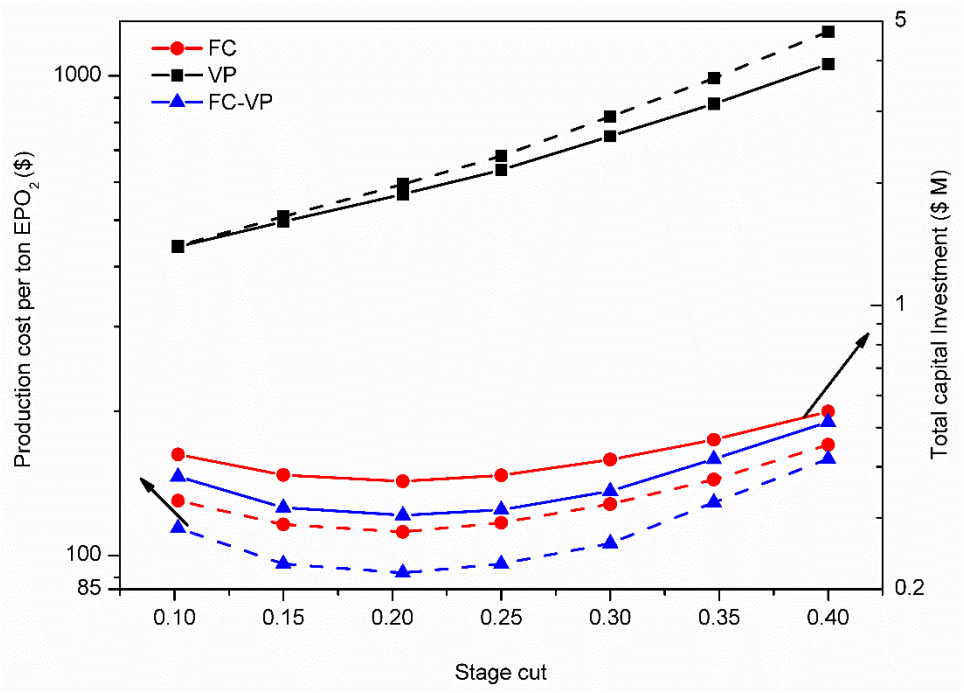

Figure 10: PC and TCI as function of stage cut, O_2 permeability: 200 Barrer, O_2/N_2 selectivity: 18

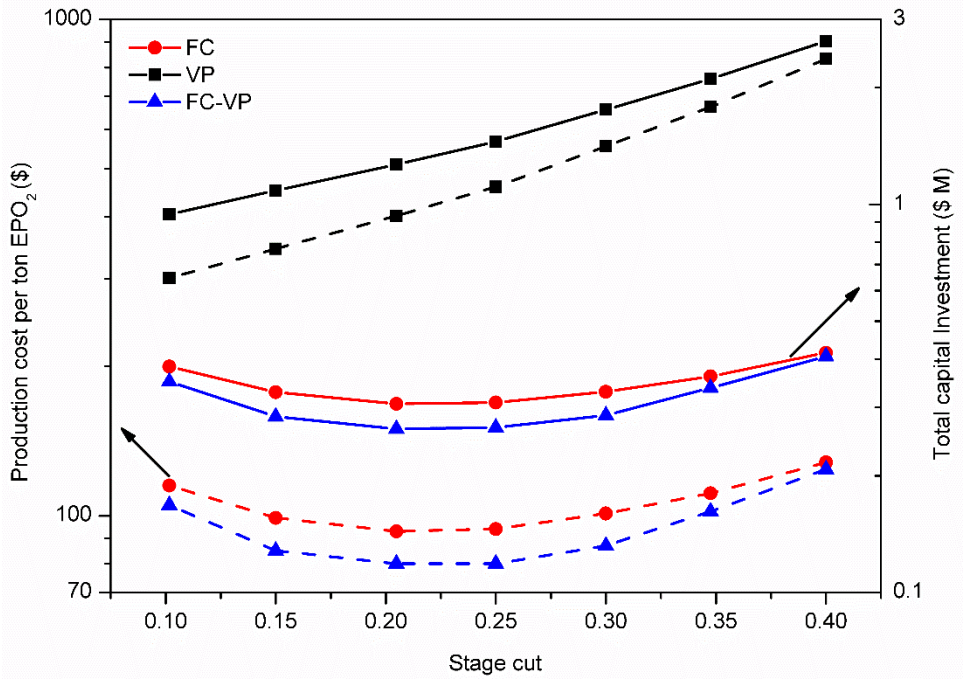

Figure 11: PC and TCI as function of stage cut, O_2 permeability: 300 Barrer, O_2/N_2 selectivity: 18

The plots in figure 12 demonstrate the lowest PC cost per ton of EPO_2 (bar chart) and TCI (scatter plot) for different compression approaches at optimal stage cut and different permeability values. Results show FC-VP approach is the most efficient approach to produce

EPO_2 economically for the CM discussed here. This approach can produce a ton of EPO_2 below $ 100 if the membrane permeability is 200 Barrer and O_2/N_2 selectivity of 18, and this performance can be accomplished either operating the membrane at 190 °C or adding nano particles to the precursor.

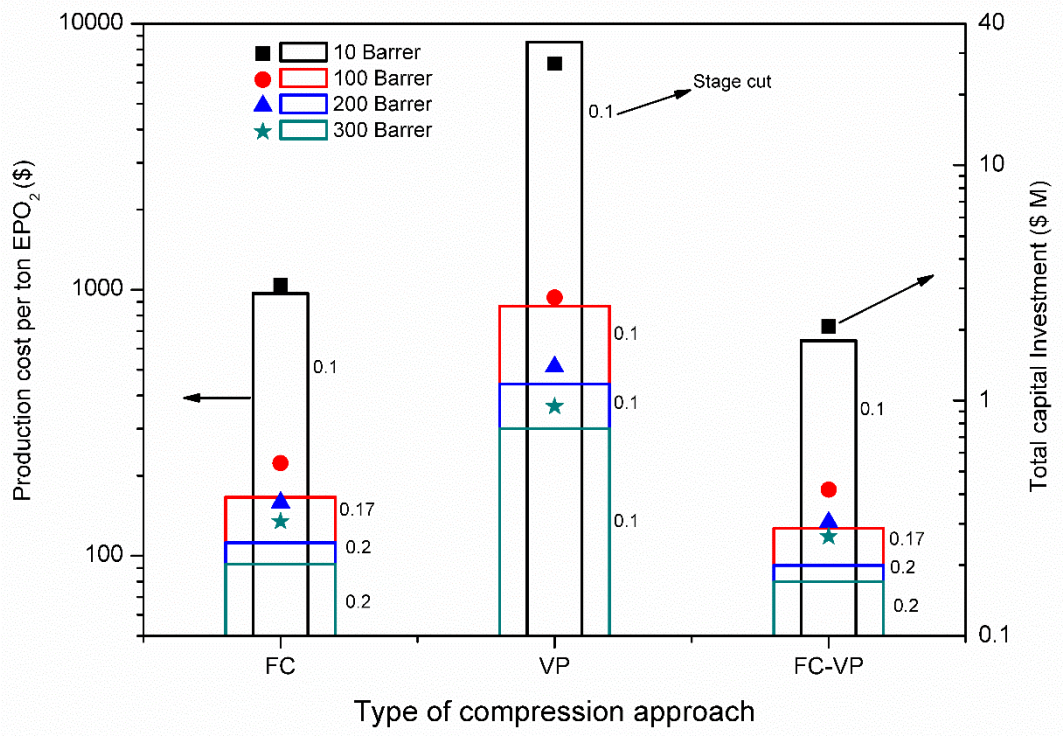

Figure 12: Lowest PC and TCI for different compression approaches at optimal stage cut value

4.3. Sensitivity analysis

Sensitivity Analysis was used to identify components that are most sensitive to achieve economically suitable results. This section presents the results of simulation analysis in which impact of different variables on TCI and PC per ton of EPO_2 is investigated and discussed. The parameters investigated here are membrane cost, membrane life time, and operating temperature which directly is related to the permeability of the membrane.

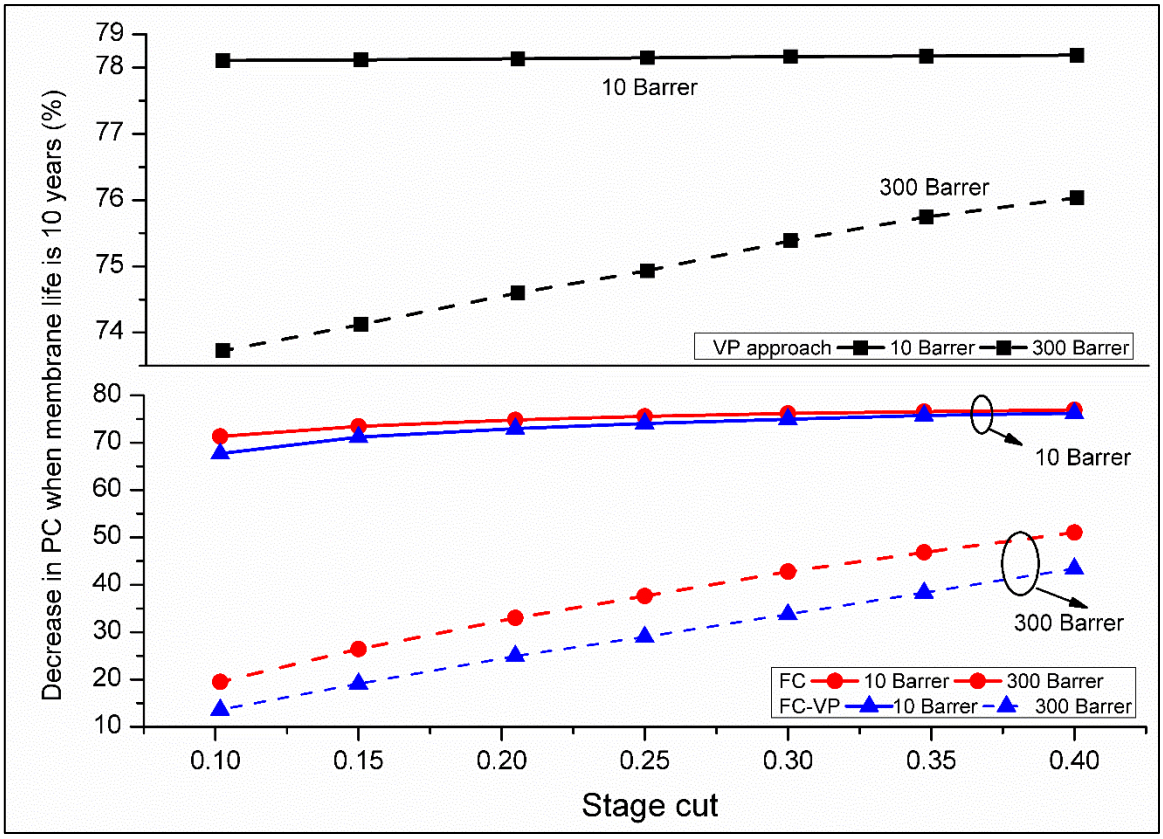

Figure 13: Effect of CM life time on PC of EPO_2 for different compression approaches (CM cost: \$100/m^2

Figure 13 presents the percent decrease in PC/ ton of EPO_2 when CM life time is increased to 10 years. The results show that production cost is significantly affected by the membrane life time while using VP approach. The production cost can be reduced 73-78% by doubling the membrane life and keeping the cost \$100 per m^2. The membrane life is considered 5 years in this study due to the challenges with mechanical properties of carbon membranes. FC and FC-VP approaches are also affected by membrane life, but the effect decreases exponentially with increase in permeability up to 300 Barrer. This effect is almost negligible at 400 Barrer as the membrane area seems fully optimized towards the production rate of EPO_2. However, in case of VP approach, the membrane area optimizes towards the production rate of EPO_2 when O_2 permeability is above 1000 Barrer.

Table 4 illustrates the sensitivity of the separation process to the membrane cost, membrane life and operating temperature which is directly related to the permeability of the membrane. VP approach is greatly affected by the membrane cost, for example the PC and TCI for this approach reduces 27 times for permeability of 300 compared to 10 by cutting the membrane cost to half. Similar trend is observed for the PC/ton of EPO_2 when membrane life is 10 years

while using VP approach. However, the TCI would remain quite high due to membrane cost of \$ 100/m^2. That is why even the PC is decreased to \$ 80 / ton EPO_2, but the TCI is about \$ 0.95 million which is not feasible. The sensitivity of FC and FC-VP approaches towards membrane cost is higher between permeability of 10-100 and beyond that the effect is very small (<10%). If the carbon membrane production process is fully optimized in future and price is reduced to \$ 50 per m^2 then PC per ton of EPO_2 can be cut to \$ 67 which presently is \$ 80 while operating at 300 Barrer.

Table 4: Sensitivity of the process towards membrane life and membrane cost (optimal stage cut for each compression)

Compression approach	Permeability (Barrer)	Membrane life (10 years, cost: \$100/m^2)		Membrane Cost (\$ 50/m^2)		Stage cut
FC		PC	TCI	PC	TCI	
	10	\$ 270	\$ 3,000,000	\$ 530	\$ 1,600,000	0.1
	100	\$ 87	\$ 540,000	\$ 120	\$ 380,000	0.15
	200	\$ 66	\$ 360,000	\$ 83	\$ 270,000	0.2
	300	\$ 63	\$ 300,000	\$73	\$ 240,000	0.2
VP						
	10	\$ 1,800	\$ 27,000,000	\$ 4,200	\$ 13,000,000	0.1
	100	\$ 200	\$ 2,700,000	\$ 440	\$ 1,300,000	0.1
	200	\$ 110	\$ 1,300,000	\$ 230	\$ 710,000	0.1
	300	\$ 80	\$ 940,000	\$ 160	\$ 490,000	0.1
FC-VP						
	10	\$ 200	\$ 2,000,000	\$ 370	\$ 2,000,000	0.1
	100	\$ 77	\$ 400,000	\$ 95	\$ 310,000	0.15
	200	\$ 62	\$ 300,000	\$ 73	\$ 240,000	0.2
	300	\$ 60	\$ 260,000	\$ 67	\$ 220,000	0.2

5. Conclusions

A single stage membrane process with no recycle stream based on O_2-selective carbon membranes was evaluated for production of OEA. Three compression approaches were simulated to economically produce one ton of EPO_2 per day with low total capital investment. In first section of the study, the experimental data were simulated to evaluate the production of EPO_2. TCI and PC were calculated based on optimal stage cut value. In the second section, the separation properties of the prepared CM were predicted to achieve high O_2 permeability, between100-300 Barrer, by keeping the selectivity constant. This improved permeability may be achieved by operating the CM and elevated temperature up to 190-205 °C. The simulation

results indicated that CM with O_2 permeability of 200 and a O_2/N_2 selectivity of 18 may produce one ton of EPO_2 in $ 92. The summary of the main conclusions of the study is shown in table 5.

As shown in table 5, CM with O_2 permeability of 300 may produce a ton of EPO_2 in $ 80, however, the retentate stream is 92.57 % N_2 which is an extra profit and that is not considered in economic analysis. This cost considers a CM price of $ 100/m^2, a depreciation rate of 10% for the plant which includes compressor, vacuum pump, valves, and piping (except membrane), and a return on investment of 12%/year. CM possess weak mechanical properties compared to polymeric membranes. Based on experience from pilot scale production, the membrane life of 5 years and prepared module cost $ 100/m^2 was considered as realistic in this study. Although vacuum pump approach requires less energy compared to cryogenic distillation, it was found that this approach is not economical as the membrane area towards the production rate is not optimal (due to too low permeability of the membrane) which resulted in very high TCI and PC of EPO_2 with current cost of membrane. However, a combined approach, feed compression and vacuum pump, may produce EPO_2 economically for the current price and life of the CM. A sensitivity analysis was performed in which different parameters like membrane cost, membrane life time, and operating temperature which are directly related to the permeability of the membrane, were investigated. The results from sensitivity analysis showed that FC-VP approach may produce a ton of EPO_2 in $ 67 if membrane life time could be increased to 10 years instead of 5.

It can be stated that even though CM is almost five times more expensive than polymeric membranes, the high performance (selectivity) and tolerance to elevated temperatures CM is a potential candidate in production of OEA and or high purity (99.5 %) N_2 in a single stage process. The present study indicates that CM process for OEA have the best potential of becoming economically competitive with conventional technologies for small plant capacities (1-10 tons/day) and a high degrees of oxygen enrichment, 50-78 mole % O_2. To be fully competitive with cryogenic distillation and PSA, the membrane cost needs to be reduced and mechanical strength of CM should be increased to maximize the life time of membrane.

Table 5: Lowest values of TCI and PC/ton EPO_2 (CM price: \$100/m^2) for different compression approaches

Compression approach	O_2 Permeability Barrer	O_2 in permeate % mole	N_2 in retentate % mole	kW/ton of EPO_2	TCI (\$)	\$/ton EPO_2
FC-VP	300	72.71	92.57	741	260,000	80
FC	300	65.68	90.51	727	310,000	93

Acknowledgement

The authors would like to thank The Department of Chemical Engineering at NTNU for providing the possibility to work with this article.

References

[1] M. Anheden, J. Yan, G. De Smedt, Denitrogenation (or oxyfuel concepts), Oil and Gas Sci. Technol. 60(3) (2005) 485-495. doi: 10.2516/ogst:2005030

[2] A.R. Smith, J. Klosek, A review of air separation technologies and their integration with energy conversion processes, Fuel Process. Technol. 70(2) (2001) 115-134. doi: http://dx.doi.org/10.1016/S0378-3820(01)00131-X.

[3] L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320(1–2) (2008) 390-400. doi: http://dx.doi.org/10.1016/j.memsci.2008.04.030

[4] B.D. Bhide, S.A. Stern, A new evaluation of membrane processes for the oxygen-enrichment of air. I. Identification of optimum operating conditions and process configuration, J. Membr. Sci. 62(1) (1991) 13-35. doi: http://dx.doi.org/10.1016/0376-7388(91)85002-M.

[5] R. Prasad, F. Notaro, D.R. Thompson, Evolution of membranes in commercial air separation, J. Membr. Sci. 94(1) (1994) 225-248. doi: http://dx.doi.org/10.1016/0376-7388(93)E0193-N.

[6] S.L. Matson, W.J. Ward, S.G. Kimura, W.R. Browall, Membrane oxygen enrichment, J. Membr. Sci. 29(1) (1986) 79-96. doi: http://dx.doi.org/10.1016/S0376-7388(00)82020-7.

[7] B. Belaissaoui, Y. Le Moullec, H. Hagi, E. Favre, Energy Efficiency of Oxygen Enriched Air Production Technologies: Cryogeny vs Membranes, Energy Procedia 63 (2014) 497-503. doi: https://doi.org/10.1016/j.egypro.2014.11.054.

[8] W.N.W. Salleh, A.F. Ismail, Carbon membranes for gas separation processes: Recent progress and future perspective, J. Membr. Sci. Res. 1(Issue 1) (2015) 2-15.

[9] C.W. Jones, W.J. Koros, Carbon molecular sieve gas separation membranes-I. Preparation and characterization based on polyimide precursors, Carbon 32(8) (1994) 1419-1425. doi: http://dx.doi.org/10.1016/0008-6223(94)90135-X.

[10] W. Shusen, Z. Meiyun, W. Zhizhong, Asymmetric molecular sieve carbon membranes, J. Membr. Sci. 109(2) (1996) 267-270. doi: http://dx.doi.org/10.1016/0376-7388(95)00205-7.

[11] J.E. Koresh, A. Sofer, Molecular Sieve Carbon Permselective Membrane. Part I. Presentation of a New Device for Gas Mixture Separation, Sep. Sci. Technol. 18(8) (1983) 723-734. doi: 10.1080/01496398308068576.

[12] H. Hatori, Y. Yamada, M. Shiraishi, H. Nakata, S. Yoshitomi, Carbon molecular sieve films from polyimide, Carbon 30(4) (1992) 719-720. doi: http://dx.doi.org/10.1016/0008-6223(92)90192-Y.

[13] J.A. Lie, M.-B. Hägg, Carbon membranes from cellulose: Synthesis, performance and regeneration, J. Membr. Sci. 284(1–2) (2006) 79-86. doi: http://dx.doi.org/10.1016/j.memsci.2006.07.002.

[14] S.Haider, A. Lindbråthen, J. A. Lie, M.-B. Hägg, Carbon membranes for oxygen enriched air – Part I: Synthesis, performance and preventive regeneration Sep. Purif. Technol. (2018) https://doi.org/10.1016/j.seppur.2018.05.014

[15] Q. Liu, T. Wang, J. Qiu, Y. Cao, A novel carbon/ZSM-5 nanocomposite membrane with high performance for oxygen/nitrogen separation, Chemical Communications (11) (2006) 1230-1232. doi: 10.1039/B516519A.

[16] J.A. Lie, M.-B. Hägg, Carbon membranes from cellulose and metal loaded cellulose, Carbon 43(12) (2005) 2600-2607. doi: http://dx.doi.org/10.1016/j.carbon.2005.05.018

[17] G. Jensen, J. G. Holmberg, A. Gussiås, Hypoxic air venting for protection of heritage, Riksantikvaren, Directorate for Cultural Heritage and Crown, 2006.
[18] S. Haider, A. Lindbråthen, J.A. Lie, I.C.T. Andersen, M.-B. Hägg, CO_2 separation with carbon membranes in high pressure and elevated temperature applications, Sep. Purif. Technol. 190 (2018) 177-189. https://doi.org/10.1016/j.seppur.2017.08.038
[19] D. Grainger, PhD. Thesis (ISBN 978-82-471-4302-5), Development of carbon membranes for hydrogen recovery, NTNU, Trondheim, 2007.
[20] M. Mulder, Basic Priciples of Membrane Technology, Kluwer Academic Publishers, Netherlands, 1996.
[21] J.A. Lie, PhD. Thesis (ISBN 82-471-7191-0): Synthesis, performance and regeneration of carbon membranes for biogas upgrading – a future energy carrier, NTNU, Trondheim, 2005.
[22] He X, Lie JA, Sheridan E, Hägg M-B. Preparation and Characterization of Hollow Fiber Carbon Membranes from Cellulose Acetate Precursors. Ind. Eng. Chem. Res. 2011;50(4):2080-7. doi: 10.1021/ie101978q.
[23] S. Haider, A. Lindbråthen, M.-B. Hägg, Techno-economical evaluation of membrane based biogas upgrading system: A comparison between polymeric membrane and carbon membrane technology, Green Energ. Env. 1(3) (2016) 222-234. doi: http://dx.doi.org/10.1016/j.gee.2016.10.003.
[24] S. Haider, A. Lindbråthen, J.A. Lie, P. V. Carstensen, T. Johannessen, M.-B. Hägg, Vehicle fuel from biogas with carbon membranes; a comparison between simulation predictions and actual field demonstration, Green Energ. & Env. https://doi.org/10.1016/j.gee.2018.03.003
[25] B.D. Bhide, S.A. Stern, A new evaluation of membrane processes for the oxygen-enrichment of air. II. Effects of economic parameters and membrane properties, J. Membr. Sci. 62(1) (1991) 37-58. https://doi.org/10.1016/0376-7388(91)85003-N