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Energy Efficiency of Oxygen Enriched Air Production Technologies: Cryogeny vs Membranes

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Abstract

Oxygen Enriched Air (OEA) is used in numerous chemical, medical and industrial applications (e.g. combustion enhancement for natural gas furnaces, coal gasification). More recently, it attracted attention for hybrid carbon capture processes. Membrane separation has shown growing interest for OEA production, providing an alternative to conventional air separation processes such as cryogenic distillation and pressure swing adsorption. Nevertheless, based on the current polymeric materials performances, membranes are usually considered to be competitive only for medium O₂ purity (25-40%) and small scale plants (10-25 tons/day).

Improvement in membrane materials permeability and permselectivity (O₂ over N₂) is often reported to be a critical issue in order to increase the attainable O₂ purity and to make the process more energy efficient. Recently, several membrane materials have been reported to show performances far above the permeability/selectivity trade-off of dense polymers. In this study, the potential of current and prospective membrane materials to achieve OEA production thanks to a single stage process is analysed through a rigorous simulation approach. The two processes (membrane and cryogenic distillation) are critically compared in terms of energy efficiency (kWh/ton O₂), depending on O₂ purity and on membrane material selectivity levels.

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1. Introduction

Oxygen enriched Air (OEA) production is used in numerous chemical and environmental applications as well as in combustion enhancement of natural gas and coal gasification. Today, the most mature technologies for O₂ production are cryogenic distillation and pressure swing adsorption (PSA). Cryogenic distillation enables to produce high purity O₂ (>99%) at a large scale (beyond 100-300 tons/day) while pressure swing adsorption (PSA) produces O₂ concentration around 95% and is suitable for small to medium scale plant (20-100 tons/day). These techniques are however still considered as too energy intensive. Membrane separation technique has shown growing interest during last decades as an alternative approach. However, currently commercially available polymeric membranes are not able to economically produce comparable O₂ purity (above 95%) in a large scale production than the conventional techniques. Nevertheless, oxygen separation membranes have been shown to be attractive and competitive for medium O₂ purity (25-40%) and small scale plant (10-25 tons/day) [1,2].

It is worth to notice that improvement of membrane materials permeability and permselectivity (O₂ over N₂) is a critical issue in order to increase the attainable O₂ purity and to make the membrane process more energy efficient [3]. Recently, novel facilitated transport membranes or carbon molecular sieves membranes have been reported showing performances far above the trade-off curve [4-6]. In this work, we focus on the potential of current and prospective membrane materials to achieve energy efficient O₂ enriched air production compared to the conventional cryogenic distillation. The most relevant process (among membrane and cryogenic distillation) in terms of energy efficiency is identified depending on O₂ purity and on the membrane material selectivity levels. To our knowledge, such a comparative study has not been reported up to now.

Nomenclature

P_{upstream}	Membrane module upstream side pressure (Pa)
$P_{\text{downstream}}$	Membrane module downstream side pressure (Pa)
P_{in}	Feed mixture pressure, fixed to 1 bar
P_{out}	Outlet pressure, fixed to 1.2 bar
ρ	Membrane permeability coefficient (mol.m ⁻¹ .s ⁻¹ .Pa ⁻¹)
Q_{in}	Inlet total flow rate (mol.s ⁻¹)
Q_{p}	Permeate flow rate (mol.s ⁻¹)
Q_{R}	Retentate flow rate (mol.s ⁻¹)
T	Temperature (K)
y	O ₂ mole fraction in the permeate (-)

Greek letters

α	Membrane selectivity (O ₂ over N ₂) (-)
γ	Adiabatic gas expansion coefficient (-)
θ	Module stage cut ($Q_{\text{p}}/Q_{\text{in}}$) (-)
ψ	Membrane module pressure ratio ($P_{\text{downstream}}/P_{\text{upstream}}$) (-)

2. Membrane materials for O₂ production

A large number of studies have been reported on polymeric materials for oxygen production. One key characteristics of polymeric membranes is their performances limitation by the permeability-selectivity trade-off as shown in Figure 1. Figure 1 shows the O₂/N₂ selectivity (α) data for different membrane materials versus O₂ permeability. The trade-off curve (i.e. the upper bound line) corresponding to a maximum polymeric membrane performance obtained through theoretical calculation, has been added.

Recently, numerous studies have been reported on new materials such as inorganic, hybrid organic-inorganic, advanced polymeric and facilitated transport membranes, showing performances far above the trade-off curve, as

reported on Figure 1. Many publications have been dedicated to membrane material development such as advanced polymeric membranes, block copolymer based membranes, cross-linked polymeric membranes, polymers with intrinsic micro porosity (PIM), facilitated transport membranes (such as liquid membranes) [6] or carbon molecular sieves membranes [5]. Despite these advanced material development, polymers only are currently used for industrial applications. In the following, the potential of current and prospective membrane materials to achieve energy efficient O₂ enriched air production will be evaluated and compared to the conventional cryogenic distillation.

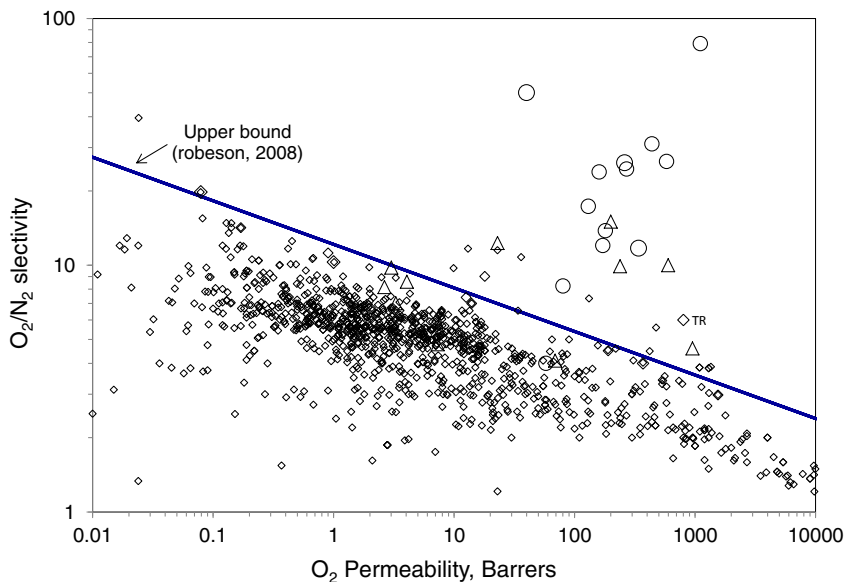


Fig. 1. Trade-off curve showing the O₂/N₂ selectivity (α) data for different membrane materials versus O₂ permeability (in Barrer), \diamond : Polymeric membranes [4], Δ : carbon molecular sieve membranes (CMS) [5], \circ : facilitated transport membranes (FTM)[6]. The theoretical trade-off limit, calculated according to Robeson (2008) for a strict physical separation mechanism (i.e. solution-diffusion) is also shown.

3. Membrane separation process

Modeling a gas separation module is based on the so-called cross-plug flow model which has been shown to offer realistic predictions of the separation performances of industrial units [7,8]. The process performances can be computed through the numerical resolution of the characteristic mass balance equations. Details of the system of equations and resolution method (based on DASSL solver in our case), can be found elsewhere [9].

From a simulation point of view, the key variables influencing the membrane separation performances are as follows:

- i) The pressure ratio ($\psi = P_{downstream}/P_{upstream}$) between the upstream and downstream compartments. It is a key operating parameter that affects both separation performance and energy requirement.
- ii) The stage cut, $\theta = Q_p/Q_{in}$, defined as the ratio of permeate flowrate to feed flowrate.
- iii) The membrane selectivity ψ corresponding to the ratio of the permeabilities of O₂ over N₂.

In this work, a single stage membrane process has been simulated for membrane selectivities ranging between $\alpha=4.5$ to $\alpha=50$, covering commercially available membranes and prospective membranes. Moreover, a systematic analysis regarding the key process parameters: the stage cut (θ); feed to product flows ratio, membrane selectivity and the compression strategy, is achieved. A diagram of a single stage membrane process is shown in Figure 2 in the

case of the strategy based on permeate vacuum pumping.

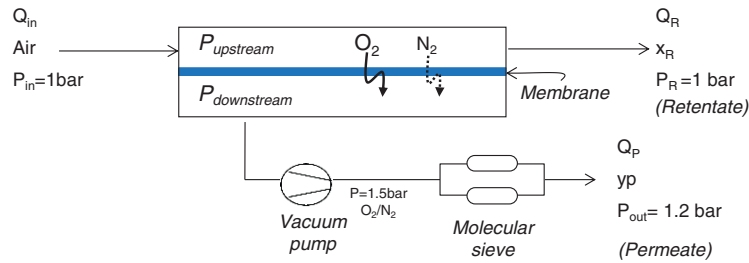


Fig. 2. Diagram of a single-stage membrane unit for air O₂ enrichment - scheme for permeate vacuum pumping strategy.

The air feed consisting of 1% water and other minor species such as CO₂ (0.03%) and Ar (0.92%) is fed to the membrane upstream compartment at atmospheric pressure. The downstream compartment is under vacuum thanks to continuous pumping. Water and CO₂ being known to permeate faster (about 30 to 50 times) than the other gases (water being the more permeable one), are therefore supposed to be almost totally recovered on the permeate side. Argon permeability is about 10 times lower compared to that of CO₂, and of the same order of magnitude than that of N₂ [10]. Consequently, argon will essentially remain in the retentate compartment. This situation is different to cryogenic separation, where Ar will be recovered in the O₂ rich stream. In the permeate side, water and CO₂ are removed from the permeate stream using pressure swing adsorption (molecular sieve). The pressure drop through the PSA (molecular sieve) is evaluated at 0.3 Bar. The regeneration step of the PSA unit can be achieved by depressurization to atmospheric pressure or using dry nitrogen as a sweep gas. The oxygen enriched permeate of the membrane unit is recovered at 1.2 Bar in order to enable a direct comparison with the outlet cryogenic product stream. The additional energy consumption of air feed or permeate purification step has been taken into account in this study in order to achieve a rigorous comparison to the cryogenic Air Separation Unit (ASU).

4. Cryogenic air separation

The specific energy consumption of a conventional cryogenic air separation unit (compressor work divided by the mass flow of produced oxygen) has been determined for different target oxygen purity values with realistic thermodynamic and technological hypotheses. The flow sheet of the air separation unit (ASU) producing gaseous oxygen at 1.2 bars is given in Figure 3.

In the ASU unit, ambient air is compressed before being purified in a pressure swing adsorption unit (molecular sieve). Afterwards, pressurized air is cooled near its dew point in the main heat exchanger by distillation products and fed in the high pressure column. Air distillation takes place in both columns and the products are recovered slightly above atmospheric pressure after being reheated in the main heat exchanger. The pressure at the end of the compression train is function of the required oxygen purity.

The ASU has been simulated for oxygen product purity ranging from 30 to 95%. For low O₂ purity production (below 60% O₂), it has been found that the minimal specific energy consumption is obtained when the high purity oxygen produced by the unit is diluted with dry ambient air, a percentage dilution of 60% was found to be an optimum. Furthermore, for oxygen purity above 95%, the reported value from Li et al., 2012 [11] has been adjusted to new specific energy consumption of current state of the art.

In order to accurately represent the cryogenic distillation process, a thermodynamic model of the ternary mixture of N₂/O₂/Ar is considered. For this purpose, the cubic equation of state of Peng-Robinson modified with the alpha function of Boston-Mathias [12, 13] has been chosen. Simulations have been performed with Aspen plus software.

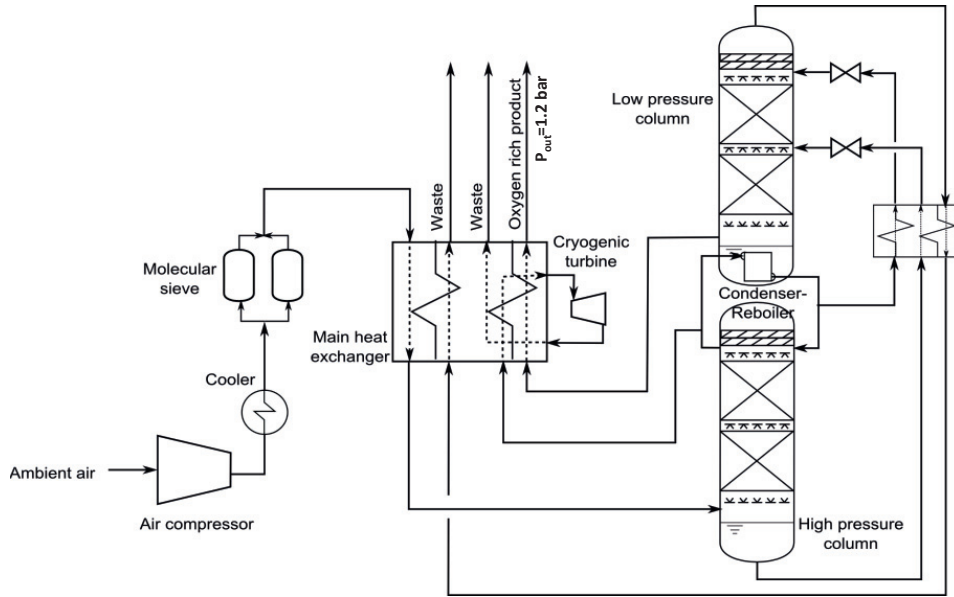


Fig.3. Flow scheme of the cryogenic distillation ASU with two thermally coupled columns

4. Results and discussion

In order to better evaluate the potential of membrane separation, the performances have been compared to a conventional cryogenic distillation. The energy requirement of a membrane unit as a function of O_2 purity is shown in Figure 4. The results are given for different membrane selectivities and for a membrane stage cut of 10%, classically considered as an average economical optimum [2].

First, it can be seen that with commercially available membranes ($\alpha=4.5$ and 6), the membrane process is competitive with the cryogenic process only for medium O_2 purity ranging between 30 to 40%, as already reported in the literature. Interestingly, with more prospective materials (α from 10 to 50), the membrane process becomes competitive for higher oxygen purity levels (i.e. 60% for $\alpha=10$ to 87% for $\alpha=50$); this could be of interest for carbon capture processes applied to oxygen enriched air combustion units [14,15].

The incidence of the air purification step (drying and CO_2 removal by molecular sieves), which is almost systematically neglected, has been more specifically investigated. Results can be found in our previous paper [16]. The results have shown that membrane performance can be overestimated, when neglecting drying and purification impacts, leading to conclusions which favor this type of membrane process technology.

More generally, these results highlight the potentialities of improved membrane materials compared to the current performances of cryogenic units. Nevertheless, it has also to be stressed that ambitious energy requirement performances (shown in red on Figure 4) are aimed for future cryogenic units, based on advanced energy integration approaches, with 150 kWh/ton O_2 for 95% O_2 as the target. In that event, cryogenic units would reach a decisive competitive status compared to membrane separation, whatever the material selectivity or oxygen purity level.

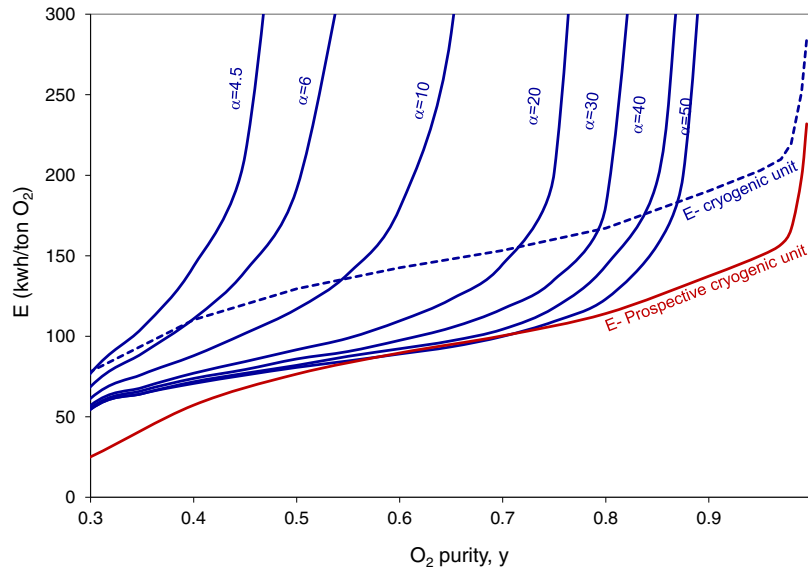


Fig.4: Energy requirement of membrane and cryogenic units as a function of oxygen purity. Membrane stage cut of $\theta=0.1$ –vacuum pumping strategy–results for different membrane selectivities. Prospective energy requirement performances for future cryogenic units have been added (red curve).

6. Conclusion

The objective of this study was to offer a rigorous comparison of membrane vs cryogenic distillation in terms of energy efficiency for oxygen enriched air production. The main conclusions of the study can be summarized as follows:

- i) When vacuum pumping strategy with permeate purification is used (Figure 2), the membrane process is not competitive for medium O_2 purity with commercially available membranes (i.e. $\alpha=4.5$ and 6). A completely different conclusion is obtained when, similarly to previous studies, the membrane permeate purification impact is not taken into account [16].
- ii) With prospective membranes (α from 20 to 50), membranes show attractive energy efficiency performances for medium oxygen purity levels (35 to 70 % O_2). This could be of interest for carbon capture processes based on oxygen enriched air combustion units [14,15].

Nevertheless, ambitious energy requirement performances are aimed for future cryogenic units based on advanced energy integration approaches. In case of success, cryogenic units would reach a decisive competitive status compared to membrane separation.

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