

# Membrane-assisted Cryogenic Distillation for Energy-efficient Argon Production from Air

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High-purity argon is produced from air by cryogenic distillation; the process is energy intensive because of the similar volatilities of oxygen and argon. This work investigates the potential to reduce the energy consumption of argon production by using membrane-assisted distillation in the crude argon column of an air separation unit (ASU). Membrane-assisted distillation flowsheets are developed and simulated in Aspen Plus®. A customised model for the membrane separation is implemented in Aspen Plus as a user-defined unit. The built-in optimisation tool in Aspen Plus is used to optimise process operating conditions and the location of the membrane unit along the distillation column with the objective of minimising the overall power demand of the process. The performance of ambient polymeric membrane separations and low-temperature carbon molecular sieve membranes separations is evaluated.

Detailed simulation and optimisation results show that membrane-assisted distillation offers considerable power savings when the membrane is placed in parallel to the distillation column. For both types of membrane material, the reduction in specific power demand (i.e. per unit of argon produced) is greatest when the membrane is placed close to the feed stage of the distillation column. A reduction in specific power demand of 12 %, relative to conventional distillation, is found for commercially available polymeric membranes. The decrease in specific power demand would be even greater (up to 32 %), if carbon molecular sieve membranes operating at low temperatures could be used.

## 1. Introduction

Oxygen, nitrogen and argon are widely used commodity chemicals in the chemicals and other industries. Cryogenic air separation is the main technology for producing of large quantities of high-purity oxygen, nitrogen and argon in gaseous and liquid forms. Argon, comprising less than 1 mol% of air, is valued for its inert behaviour, and is used extensively in lighting applications, for welding and in semiconductor manufacturing (Agrawal et al., 1989). In cryogenic air separation units (ASU), liquefied air is separated into oxygen, nitrogen and argon by distillation. Although the raw material, air, is free, its separation by distillation is highly capital and energy intensive. In particular, the 3°C difference in the normal boiling points of oxygen and argon makes it very difficult to separate argon from air by conventional distillation.

Approaches to reduce the capital and operating costs associated with ASUs can broadly be classified as those that modify the process with and without changing the process configuration. Common examples for the latter approach are: a) replacement of sieve trays with advanced structured packings; (b) use of advanced machinery (e.g. highly efficient compressors and expanders); c) use of enhanced heat exchangers with very low temperature driving forces (Castle, 2002). Approaches that make structural changes include: a) adding intermediate reboilers to distillation columns (Fu and Gundersen, 2012); b) introducing advanced integrated heat recovery options to reduce energy consumption, e.g. using a heat engine to recover waste heat from the compressor (Aneke and Wang, 2015) or applying self-heat recuperation, and thus eliminating the condenser–reboiler in the ASU (Fu et al., 2014). Another approach, with great potential for separating close-boiling components oxygen and argon, is membrane-assisted distillation. The synergistic effects of membrane-assisted distillation, compared to its conventional counterpart, have been investigated in numerous theoretical and experimental studies, mainly for close-boiling and azeotropic mixtures (Etoumi et al., 2014; Wankat and

Kostroski, 2010). These studies have shown that the integrated (also known as 'hybrid') arrangement can bring substantial operating and investment cost savings, relative to conventional distillation. Etoumi et al. (2014) developed a systematic approach for synthesis and optimisation of membrane-assisted distillation schemes for close-boiling ethane–ethylene mixtures and found that the total operating cost of configuration with the membrane operating in parallel with the column is 11 % less than that of the stand-alone distillation process. Wankat and Kostroski (2010) studied a serial configuration for air separation units producing oxygen, where the membrane is used to pre-concentrate oxygen in the air to reduce the equipment size and energy consumption of the process. They have found that the membrane-assisted process applying carbon molecular sieve membranes requires less power per unit of oxygen, compared to cryogenic distillation alone, and has potential to increase production capacity to meet peak oxygen requirements. Although membrane gas separation is a relatively immature technology, it has been demonstrated to be a viable alternative to conventional distillation in a number of large scale applications such as hydrogen recovery and nitrogen production, bringing benefits related to its lower energy consumption, compactness and flexibility (Koros and Mahajan, 2000). Despite these advantages, the potential of membranes for gas separation has not been fully realised in industrial practice, mainly due to lack of membrane materials with high fluxes and long life-times (Koros and Mahajan, 2000). It is anticipated that recent progress in the development of high-performance membrane materials, will overcome these barriers and that membrane-assisted distillation processes will become more widely applied industrially (Ploegmakers et al., 2013).

The aim of this study is to evaluate the performance of membrane-assisted distillation for argon production from an air separation unit, compared to conventional cryogenic distillation. Evaluation of the overall ASU is highly complex because of the intense process integration; therefore the problem is decomposed to consider only the units separating argon from an argon-enriched side-draw from the low pressure column of the ASU. This paper explores membrane-assisted flowsheet variants through modelling, simulation and optimisation in Aspen Plus to identify the best process structure and operating conditions. Since energy costs are the dominant cost for air separation units, the specific power demand of the process (per unit of argon produced) is used as the performance indicator. Two promising classes of membrane materials identified through an extensive literature review – polymeric and carbon molecular sieve membranes – are considered in this study. The impact of membrane properties on performance is also investigated, to guide future research and development of tailored membrane materials.

## 2. Process overview

Conventionally, air is separated into nitrogen and oxygen by distillation in a double-effect column with heat exchange in an integrated condenser–reboiler. A fraction of argon-rich vapour in the low-pressure column is withdrawn and fed to an argon column to recover high purity argon. The argon-rich feed typically contains 10 mol% argon, ppm levels of nitrogen and oxygen. In the argon column, the relatively volatile argon is concentrated at the top of the column, while the oxygen concentrates at the bottom. The column condenser is cooled by the liquid stream leaving the base of the high-pressure column of the double-effect column (Agrawal and Herron, 2000).

This study uses membrane materials reported in the open literature and patents, and selects promising materials, based on their reported selectivity and permeability performance, operating conditions and technical maturity. The two types of materials selected are polymeric membranes that must operate at ambient temperatures (to avoid freezing) and carbon molecular sieve (CMS) membranes that can operate at low temperatures. The first type includes commercial polymeric materials that show moderate or low permeability with low selectivity for oxygen over argon (Haraya and Hwang, 1992). As polymeric membranes are widely used in industry for gas separations, including for oxygen–nitrogen separation, they are considered in this study. A disadvantage of using polymeric materials is that process streams to and from the membrane require heating and recooling. By contrast, the selectivity of CMS membranes actually improves at lower temperatures; for instance, the O<sub>2</sub>/Ar selectivity of a CMS membrane is 5.5 at 28 °C and 50 at –169 °C (Soffer et al., 1997), compared to 2.5 for a polymeric membrane at ambient temperature (Haraya and Hwang, 1992).

A distillation column and membrane separation unit can be combined in numerous ways which can be broadly classified according to the position of the membrane along the column; these are known as top, bottom, parallel and sequential configurations (Kreis and Górak, 2003).

This study investigates the parallel configuration (Figure 1) where a side-stream from the column feeds the membrane and membrane product streams – retentate and permeate – are returned to the column. For close-boiling mixtures such as oxygen and argon, the parallel configuration has shown good potential for performance improvements (Kreis and Górak, 2003) and the membrane is not required to produce a high-purity product. The parallel hybrid configuration also offers good flexibility for design, compared to other configurations, and has a relatively large range of operating conditions for the membrane and distillation units.

Screening such a wide design space to identify energy-efficient solutions is a challenging task; therefore this work presents a systematic approach to evaluate alternative designs.

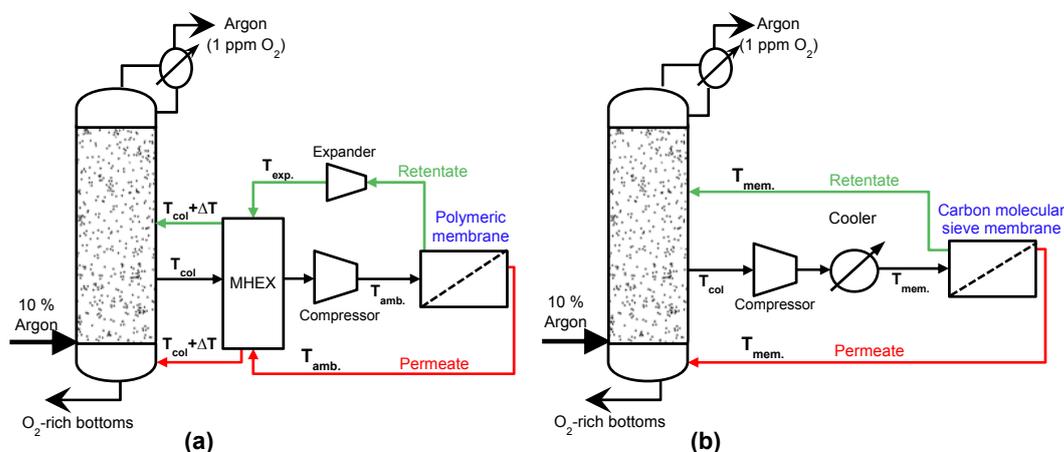


Figure 1: Process flowsheet for membrane-assisted distillation process with (a) ambient temperature polymeric membranes (b) low temperature carbon molecular sieve membranes.

### 3. Modelling and optimisation methodology

In this study, membrane-assisted cryogenic distillation flowsheets are modelled and systematically evaluated using rigorous process models in Aspen Plus. Peng Robinson equation of state is used to calculate the physical properties of the air. The optimisation tool in Aspen Plus is used to optimise the operating conditions (continuous variables) for each user-defined set of membrane and column feed locations; this approach provides consistency in the evaluation of flowsheet variants while selecting the best locations for the membrane and column feed. The simulation and optimisation framework is presented in Figure 2. First, the stand-alone argon column, which is later used in membrane-assisted flowsheet variants, is designed using *RadFrac* distillation model and evaluated, to provide a benchmark. The number of theoretical stages in the column is kept constant in all simulations. To allow design and simulation of the membrane separation, a tailored membrane simulation subroutine applies the model of Shindo et al. (1985) for multicomponent crossflow permeation. The model equations and solution algorithm, described by Ceylan et al. (2017), are embedded in a Fortran subroutine that is linked to Aspen Plus. The temperature-dependence of carbon molecular sieve membrane selectivity is represented in this model using a non-linear correlation regressed from published data.

The flowsheets with polymeric and CMS membranes (illustrated in Figure 1) differ due to their different membrane operating temperatures. For polymeric membranes, a multistream heat exchanger (MHEX in Figure 1) before the compressor preheats the membrane feed while cooling the membrane products; the compressed feed is then cooled to ambient temperature using cooling water (not shown in Figure 1a). The retentate stream is expanded, generating power for refrigeration, before being returned to the column. For CMS membranes, as shown in Figure 1b, the membrane feed is compressed and then cooled, to maintain the desired low temperature. Again, the pressure of the retentate needs to be reduced to before it is returned to the column. However, liquid would form in an expander, so an isenthalpic expansion valve is used instead.

To simplify the analysis, the argon column subsystem is evaluated; however, decoupling the argon column from the ASU means that the total compression power demand of overall system cannot be evaluated explicitly. Therefore, this work, following Agrawal et al. (1989), assumes that 1 W of compression power produces 0.35 W of cooling at the column condenser temperature ( $-184\text{ }^{\circ}\text{C}$ ). The total power demand of the membrane-assisted flowsheet is then calculated by Eq. (1), when polymeric membranes are used, and by Eq. (2) when CMS membranes are used:

$$W_{\text{Total}} = W_{\text{Cond}} + W_{\text{Comp}} - W_{\text{Exp}} \quad (1)$$

$$W_{\text{Total}} = W_{\text{Cond}} + W_{\text{Comp}} + W_{\text{Cool}} \quad (2)$$

where  $W_{\text{Cond}}$  is the equivalent power demand of the column condenser,  $W_{\text{Comp}}$  is the membrane feed compressor power demand,  $W_{\text{Exp}}$  is the power generated by the retentate expander and  $W_{\text{Cool}}$  is the equivalent power demand of the membrane feed cooler.

The operating variables to be optimised for the flowsheets shown in Figure 1 are the membrane feed flow rate, transmembrane pressure ratio and membrane stage cut. There are also four structural degrees of freedom, namely the locations of three feeds to the column (including the membrane products) and the stage from which the membrane feed is withdrawn. The influence of operational and structural parameters on the total power demand was investigated with preliminary sensitivity analyses, results for which are not presented. These sensitivity analyses showed that increasing the pressure ratio, increases the total power demand but reduces membrane area requirements, implying a trade-off between capital and operating costs. As this study focuses on energy demand, the pressure ratio is excluded from the optimisation, but selected through parametric studies.

The optimisation problem is solved using the built-in non-linear optimisation tool in Aspen Plus, using sequential quadratic programming. The objective is to minimise total specific power demand; the objective function is coded in Fortran (within the optimisation tool). As the non-linear solver cannot optimise discrete variables, the feed and draw locations – column feed stage ( $S_C$ ), side draw stage ( $S_M$ ), and retentate and permeate return stages ( $S_R$  and  $S_P$ ) – are specified, and the optimisation is run for each set of specifications. The purity of the argon product is specified directly in Aspen Plus (rather than within the optimisation problem), where the reflux ratio is the manipulated variable. The constrained optimisation problem is represented by:

$$\min. f(\theta, F_{\text{MEM}}) = \frac{W_{\text{Total}}}{F_{\text{AR}}} \quad (3)$$

$$\text{s.t. Purity}^{\text{O}_2} < 1 \text{ ppm in distillate} \quad (4)$$

$$\theta_L \leq \theta \leq \theta_U \quad (5)$$

$$(F_{\text{MEM}})_L \leq F_{\text{MEM}} \leq (F_{\text{MEM}})_U \quad (6)$$

where  $\theta$  is the membrane stage cut (U and L are upper and lower bounds, respectively),  $F_{\text{MEM}}$  is the membrane feed molar flow rate.

#### 4. Case study and results

The methodology above is applied to a crude argon column of a typical ASU producing steel grade argon (<1 ppm  $\text{O}_2$ ). The vapour-phase column feed composition is 90 mol% oxygen, 10 mol% argon, 10 ppm  $\text{N}_2$ . The column bottom and top pressures are 1.3 and 1.2 bar, respectively. The pressure ratio across the membrane is 10 and the permeate pressure is 1.3 bar. The distillation column has 150 theoretical stages. The isentropic and mechanical efficiencies of compressor and expander are 80 % and 90 %, respectively; the minimum temperature approach in heat exchangers is 3 °C; the compressor has 4 stages of equal pressure ratio, with interstage cooling to 31 °C using cooling water.

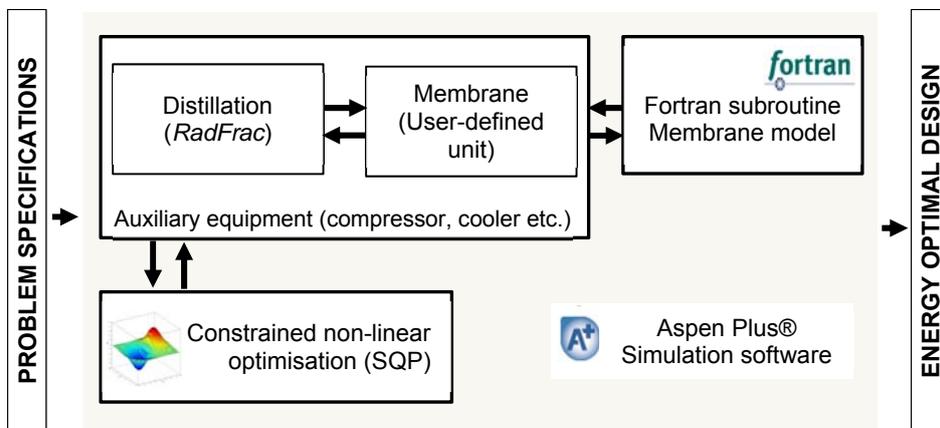


Figure 2: Simulation and optimisation framework membrane-assisted distillation flowsheets.

#### 4.1 Polymeric membrane-assisted distillation

The flowsheet structure shown in Figure 1a, with a single stage membrane unit operating at 30 °C, is optimised for four hypothetical polymeric membranes, with selectivities ( $\alpha$ ) ranging from 2.5 to 20, covering the range reported for commercially available polymeric membranes. For each membrane and each set of locations of feed and draw streams, the stage cut and membrane feed flow rate are optimised. The best location of the membrane is found to be close to the column feed stage, irrespective of the selectivity (results are not shown here) and the highest savings are achieved when the composition of the permeate and retentate feed stages and the corresponding streams are similar.

As shown in Table 1, due to synergy between the membrane unit and distillation column, the membrane-assisted process recovers more argon and has a lower specific power demand than the stand-alone column. For the same amount of argon product as a stand-alone column, less column feed has to be processed due to higher argon recovery. With a polymeric membrane with low selectivity ( $\alpha = 2.5$ ), the power demand can be reduced by 12 %. For membranes with higher selectivity, further reductions in power demand are obtained: savings increase from 12 % to 24 % when the selectivity doubles from 2.5 to 5, but further increases in selectivity yield lower additional benefits. Due to the inverse relationship between permeability and selectivity for polymeric materials, membrane area increases significantly with increasing selectivity. The membrane areas shown in Table 1 are calculated using data available for two polymeric materials with  $O_2/Ar$  selectivities of 2.4 (PPO: poly(2,6-dimethyl-1,4-phenylene oxide) and 18 (cellulose nitrate) and permeabilities of 11.4 and 1.95 barrer, respectively (Haraya and Hwang, 1992). These results imply that a moderately selective membrane might be more cost effective than a highly selective one when the cost of the membrane unit is taken into account.

#### 4.2 Carbon molecular sieve membrane-assisted distillation

The same methodology is applied to the CMS membrane-assisted flowsheet shown in Figure 1b. The effect of the temperature dependence of the selectivity of the CMS membrane is explored through parametric studies. The experimental data of Soffer et al. (1997) are used to regress non-linear correlations for the selectivity and permeability with temperature (not presented here).

As the operating temperature of the membrane approaches that of the column draw stage (–180 °C), the membrane selectivity increases, argon recovery increases and specific power demand for column condenser decreases. However, the compression power demand associated with the membrane feed cooler increases as the membrane temperature decreases. Therefore, there is an optimum operating temperature for the CMS membrane. Savings are greatest when the CMS membrane with a selectivity of 23 is operated at –120 °C. Compared to the stand-alone column, the argon recovery increases by 98 % and the specific power demand decreases by 32 %. As for polymeric membranes, the best location for the membrane is close to the column feed stage.

Table 1: Optimisation results for polymeric membranes with selectivities of 2.5–20 and CMS membrane.

Type	Polymeric membrane				CMS
Selectivity, $\alpha$	2.5	5	10	20	23
Membrane operating temperature (°C)	30	30	30	30	–120
Membrane stage cut ( $\theta$ )	0.73	0.81	0.84	0.88	0.91
Relative membrane feed flow rate <sup>a</sup>	0.43	0.39	0.37	0.41	0.64
Area <sup>b</sup>	1.0	–	–	8.4	1.1
Relative column feed flow rate <sup>c</sup>	0.75	0.68	0.65	0.61	0.50
Increase in argon recovery (%) <sup>c</sup>	34 %	46 %	54 %	64 %	98 %
Specific power savings (%) <sup>c</sup>	12 %	21 %	25 %	28 %	32 %

<sup>a</sup> Membrane feed flow relative to column feed flow.

<sup>b</sup> Membrane area is relative to that for a polymeric membrane with a selectivity of 2.5.

<sup>c</sup> Flow rate, recovery and power savings are relative to the stand-alone distillation column.

#### 4.3 Comparison of membrane types

As can be seen in Table 1, the highest specific power savings (32 %) are achieved with low temperature operation of CMS membrane-assisted distillation. The performance of a highly selective ( $\alpha = 20$ ) polymeric membrane is similar in terms of power savings (28 %), even though the heating and cooling is needed to operate the membrane at ambient temperature. However, as shown in Table 1, the selectivity and permeability trade-off that applies to polymeric materials implies an 8-fold increase in membrane area, rather

than a 10 % increase for the CMS membrane. Therefore, it can be concluded that emerging CMS membranes are very promising for membrane-assisted distillation for argon production. To date, CMS membranes suffer from poor mechanical properties and are not yet commercialised (Li et al., 2011). Polymeric membranes, which are more mature and cheaper, also offer significant energy benefits, especially if further research and development can enhance their permeability, and thus decrease their area requirements. It is also noted that, for new design of membrane-assisted distillation processes, the capital cost of the argon column could be significantly reduced, because less feed would need to be separated for a given argon production rate.

## 5. Conclusions

This study evaluated a parallel configuration of membrane-assisted distillation for energy-efficient production of argon from air. A systematic approach is used to the best location for the membrane along the column and to optimise the operating conditions using Aspen Plus. The results show that specific power demand (i.e. per unit of argon) can be reduced, compared to conventional distillation, by 28 to 32 % using highly selective polymeric membranes or carbon molecular sieve membranes. Further work aims to explore the integrated flowsheet more fully and to develop an approach for new design of membrane-assisted distillation, considering the number of stages in the distillation column and additional energy integration opportunities within the ASU.

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