

## Intensifying Air Separation Units

Flavio Manenti<sup>a,\*</sup>, Francesco Rossi<sup>a</sup>, Giulia Croce<sup>a</sup>, Maria G. Grottoli<sup>b</sup>,  
Marcello Altavilla<sup>c</sup>

<sup>a</sup>Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Piazza Leonardo da Vinci 32, 20133 Milano, Italy

<sup>b</sup>Fondazione Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

<sup>c</sup>Linde Gas Italia S.r.l., Operations Division, Terni Plant, Viale Benedetto Brin 214, 05100 Terni, Italy  
flavio.manenti@polimi.it

This research activity shows the possibility to further intensify air separation units (ASUs). Several modifications to the traditional process layout are proposed and simulated by means of well-established simulation suites. The proposed modifications deal with the upgrading of oxygen purity, the recycle of rich argon stream, and the possibility to generate energy. The novel process solutions are compared with the traditional process and techno-economic assessment is provided. The payback time on the revamping investment is estimated in the order of 5 years for Terni's ASU, owned by Linde Gas Italia S.r.l., which has been selected as test-case.

### 1. Introduction

Air separation units (ASUs) are energy-intensive plants for the production of nitrogen, oxygen and argon with different qualities. The layout of ASUs usually consists of a compression section, a refrigeration section and a separation section where the air is separated into its main compounds with different specifications according to the market requirements (i.e. health/hospital, steel mills, oil refineries...). There is a wide literature on the management of ASUs and the definition of optimal operating conditions (Marangoni et al., 2011) according to the energy price volatilities (D'Isanto et al., 2011) and the market fluctuations (Jiang et al., 2003) and recently by (Huang et al., 2009) and demand peaks (Zhu et al., 2001). Conversely, much less works are dedicated to the improvement of process layout because of the assumption that the optimization degree achieved on these plants is rather high. This research activity, developed in collaboration with Linde Gas Italia S.r.l., is aimed at investigating in detail the behavior of an existing ASU and at assessing the effectiveness of an intensified layout in terms of production capacity, product quality, and energy recovery/consumption (Smith and Klosek, 2001). To do so, the detailed process simulation of the overall ASU operating in Terni (Italy) is developed and sensitivity analysis is given for main parameters (Section 2). Total-plant process-energy intensifications have been proposed (Section 3). Economic benefits are estimated using net present value and payback studies (Section 4).

### 2. Process

#### 2.1 Process flow diagram description

The typical block flow diagram (BFD) of air separation units currently operating worldwide is reported in Figure 1. It consists of three main sections: compression, refrigeration, and separation. The first includes the main air compressor, two water refrigerators, and the molecular sieves (not reported in the BFD because of our simulation assumption of only argon, nitrogen, and oxygen as inlet air components). The refrigeration section includes the refrigeration cycle (with a coaxial compressor, an alternative compressor, and a turbine), the main heat exchanger, and the sub-cooler (placed downstream the first two columns). The separation section consists of three distillation towers. The first is the Linde fractionator, which is modeled using two separate columns to represent its High Pressure (HP) and Low Pressure (LP) portions. The last two columns of the BFD have the task to separate the argon from oxygen (T4111) and the argon

from nitrogen (T4112). The overall process simulation involves 51 models of process units and 87 streams leading to a very large-scale nonlinear system. The simulation is solved using the commercial process simulator PRO/II by Simulation Science (Simsci-Esscor, 2002).

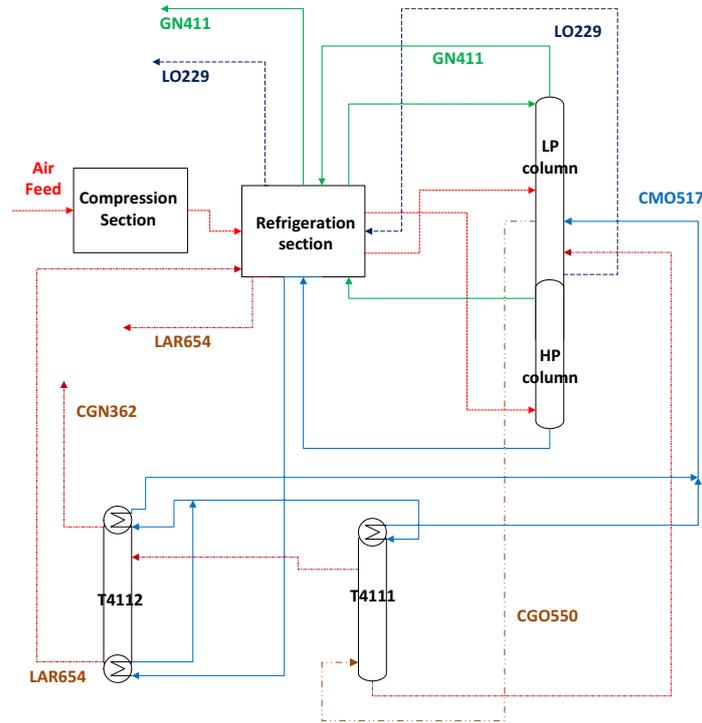


Figure 1: Simplified Block Flow Diagram of Terni's ASU. It is a typical layout of air separation units.

## 2.2 Sensitivity Analysis

Air separation units are commonly subject to relevant production variations according to the energy availability (Park et al., 2006) and to the market demand dynamics (Manenti et al., 2013), beyond the planned/unplanned plant maintenance that could limit the same production. Thus, the sensitivity of the system has been studied in order to assess the operating conditions of the ASU under different production scenarios. Some interesting results have been obtained varying the oxygen molar fraction recovered from LP column (Figure 2 to Figure 4) in the range of 0.9900-0.9999 (the typical condition is 0.9979) and using 3 different pressure sets. Parameters are summarized in Table 1. In Figure 2, the connection between the molar fraction of the produced argon  $X_{Ar}$  LAR654 and the molar fraction of the produced LP oxygen  $X_{O_2}$  LO229 is reported. It can be clearly seen that  $X_{Ar}$  decreases with the increase of  $X_{O_2}$ . For an oxygen molar fraction greater than 0.998, the argon molar fraction collapses. As result, the argon is no anymore at the required specification for sale. Figure 3, instead, highlights that oxygen flow is inversely proportional to its purity; this is a common behavior in many distillation columns. In Figure 4, the effect of oxygen purity on the variation of the argon flow value is shown; the argon flow increases with oxygen molar fraction; this is due to the argon material balance: when  $X_{O_2}$  LO229 increases, the amount of argon in LO229 decreases and, consequently, the flow of LAR654 increases. Although separation efficiency is expected to increase lowering column pressure, it can be noticed in all the proposed trends (Figure 2 to Figure 4) that the effect of such a parameter is negligible.

Table 1: Pressure sets

Trend index	HP Pressure [bar]	LP Pressure [bar]	T4111 Pressure [bar]	T4112 Pressure [bar]
A	5.2650	1.3640	1.2750	1.2420
B	5.2650	1.2697	1.1735	1.1486
C	5.2650	1.1594	1.0704	1.0557

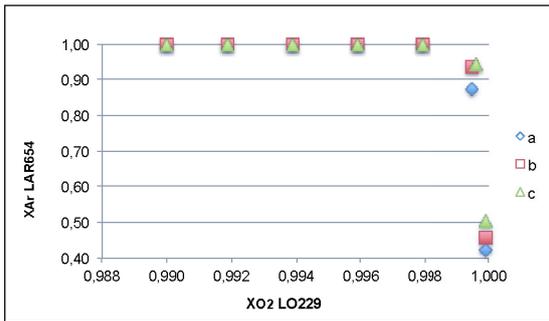


Figure 2: Ar and O<sub>2</sub> purity

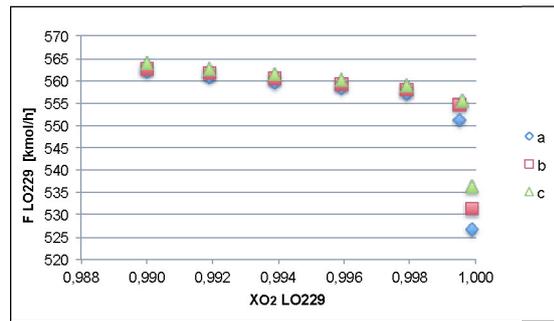


Figure 3: O<sub>2</sub> flow and O<sub>2</sub> purity

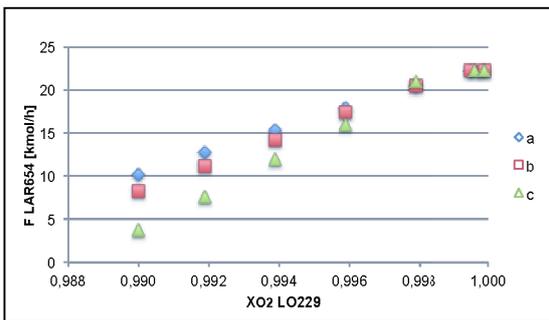


Figure 4: Ar flow and O<sub>2</sub> purity

### 3. Proposed process revamping

#### 3.1 Oxygen purity upgrade and fulfillment of argon purity

The economic value of each separation product depends on its degree of purity. In ASUs, the oxygen has market from a purity of 99.8% (called the O<sub>2</sub> 2.8). A typical purity is the O<sub>2</sub> 3.5 (standing for a 99.95 % of purity). A revamping procedure could have the target of increasing the economic value of oxygen production, through an increment of its molar fraction to 0.9995; unfortunately, as shown in Section 2, this would lead to a lower purity of argon that would not fulfill market specifications. To overcome this problem, a possible strategy is to shift the concentration profiles within the LP column. Actually, whenever the LP column undergoes the new specification of oxygen molar fraction of 0.9995, the argon concentration profile is significantly shifted as reported in Figure 5. Case 1a stands for the initial working point (with oxygen production at 0.9979 purity), whereas Case 1b stands for the novel working point (with oxygen production at 0.9995 purity). The maximum concentration of argon migrates from the column stage 46 to the stage 36. Consequently, it is necessary to shift the LP column side stream CGO550, which is sent to the tower T4111, from stage 46 to stage 36 (Figure 6, Case 2). By doing so, argon production enters the tight market specifications, but the molar fraction of nitrogen in the side stream CGO550 increases. As a result, the overall argon production decreases as illustrated in Table 2. The reason lies in the increasing nitrogen molar fraction of CGO550. Since in T4112 the vent (CGN362) of the argon molar fraction is assigned due to the minimum temperature constraint in the condenser, the vent unavoidably increases. This causes a sensitive reduction of LAR654 flow (at the bottom of tower T4112). To avoid this argon loss, it is suitable to shift the inlet stage of the stream CMO517, which is one of the feeds of the LP column and specifically the air recycle coming from the condensers of the argon towers (T4111 and T4112). It is therefore crucial to decouple the profile of nitrogen from the argon profile. This is finally possible by moving the inlet stage from the 30th to 24th stage. Actually, the effect of this modification is the shift of the nitrogen concentration profile towards the top of the column (Figure 6, Case 3).

#### 3.2 Recycle of argon vent

In the standard configuration, CGN362 is released to atmosphere. Since the target is to improve the argon recovery, in the revamped configuration, CGN362 is recycled to the LP column, after a recompression. Please note that the pressure difference between T4112 and the LP column is rather small and of the order of 0.12 bar, thus, the recompression can be achieved with a blower, without any relevant additional

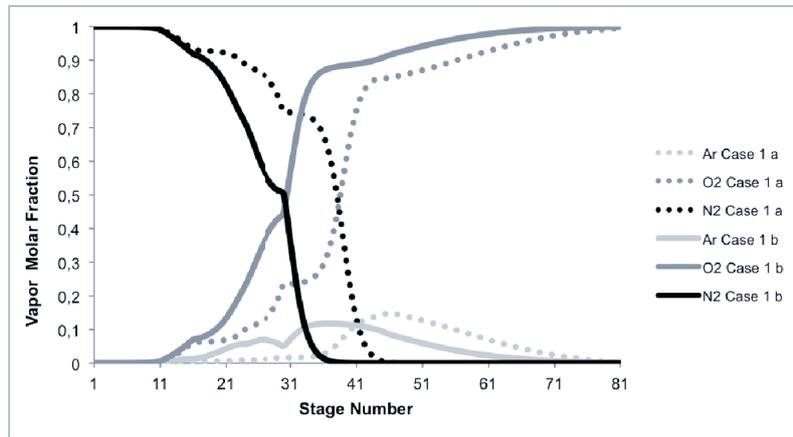


Figure 5: Concentration profiles of Ar, O<sub>2</sub> and N<sub>2</sub> (vapour phase) along the column stages (Case 1).

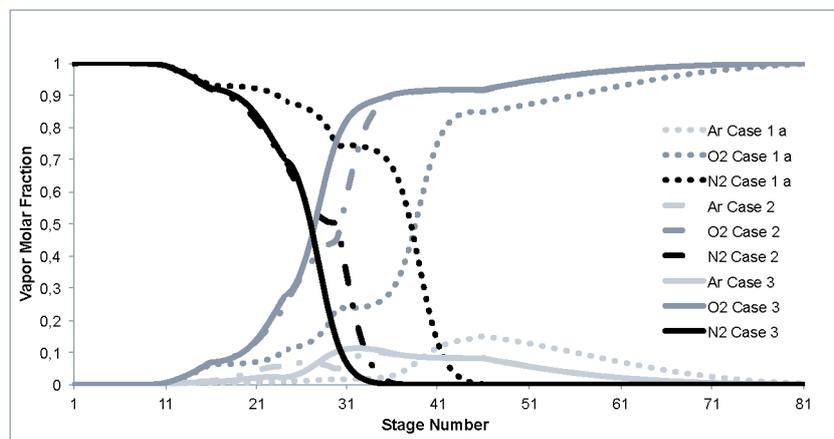


Figure 6: Comparison of concentration profiles of Ar, O<sub>2</sub> and N<sub>2</sub> (vapour phase) along the column stages.

operational cost. This new feed enters the column at the stage 35. This inlet stage has been identified with the aim to maximize argon production. The estimated improvement in argon recovery is of the order of 3%. All relevant data are given in Table 2.

Table 2: Data comparison among cases 1a, 1b, 2, 3

	Case 1a	Case 1b	Case 2	Case 3
F LO229 [kmol/h]	557.142	551.335	554.15	554.657
X <sub>O<sub>2</sub></sub> LO229	0.9979	0.9995	0.9995	0.9995
F LAR654 [kmol/h]	20.457	22.241	15.786	21.151
X <sub>Ar</sub> LAR654	0.9998	0.8737	0.9999	0.9998
Argon Recovery* [%]	0.729	0.692	0.563	0.754
Net power [MW]	-	-	-	0.316
CGO550 Inlet Stage	46	46	36	36
CMO517 Inlet Stage	30	30	30	24

\*The air feed is 2806,242 [kmol/h]; the adopted pressure set is A.

### 3.3 Energy intensification

An important focus has also been given to the energy intensification. At Terni's ASU, the oxygen is produced only in gas phase, hence it is vaporized in the main heat exchanger (LO229 is the bottom of the LP column). An economic improvement could be obtained by pumping a liquid, which is much cheaper than compressing gas: LO229 can be pumped to 120 bar, instead of current pressure of 32 bar required for gas oxygen, and the vapor phase coming from the main exchanger can be expanded into a turbine to

32 bar, generating energy. The power generation at the turbine purified by pumping costs is reported in Table 2. The overall process flowsheet adopted to test the proposed revamping solutions is reported in Figure 7. For the sake of conciseness, only the names of the main unit operations are explicitly reported.

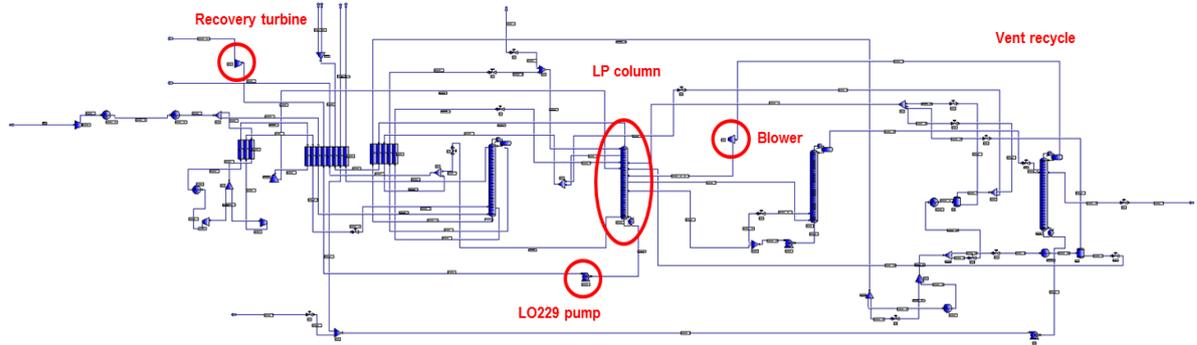


Figure 7: Overall process flow diagram after intensification.

#### 4. Economic analysis

To prove the real advantage of the proposed revamped layout, an economic analysis has been carried out. This analysis is based on the Net Present Value (NPV) method according to Ydstie's directives (Ydstie, 2004) and takes into account the Pay-Back Time (PBT). To calculate the NPV, an estimation of the additional fixed costs and as well as of the additional revenues is required. The only relevant fixed cost related to the revamped layout deals with the turbine (TC):

$$TC[\text{€}] = \frac{517.5 \text{ M \& S}}{\text{\$€}} TP_{hp}^{0.82} (2.11 + F_c) \quad (1)$$

On the other hand, the additional revenues come from:

- the increased production of argon ( $\Delta R_{Ar}$ ):

$$\Delta R_{O_2} \left[ \frac{\text{€}}{\text{y}} \right] = y_{wt} \left( F_{LO229,3} \text{€}_{3,5}^{O_2} - F_{LO229,1a} \text{€}_{2,8}^{O_2} \right) \quad (2)$$

- the higher oxygen purity ( $\Delta R_{O_2}$ ):

$$\Delta R_{Ar} \left[ \frac{\text{€}}{\text{y}} \right] = y_{wt} \left( F_{LAR654,3} - F_{LAR654,1a} \right) \text{€}^{Ar} \quad (3)$$

- and from the power generated by the turbine ( $R_{energy}$ ):

$$R_{energy} = y_{wt} TP \text{€}_{energy} \quad (4)$$

As a result, the NPV is stated as follows:

$$NPV [\text{€}] = \sum_{j=1}^{y_A} \left[ \frac{1}{(1+i)^j} \left( \Delta R_{O_2} + \Delta R_{Ar} - \frac{TC}{y_A} \right) + R_{energy} \right] - TC \quad (5)$$

Table 3: Data for economic analysis

M&S	1536	F <sub>c</sub>	1.15
\\$€	1.3	y <sub>wt</sub> [h/y]	8160
i [%]	7.5%	y <sub>PL</sub> [y]	20
y <sub>A</sub> [y]	10		
€ <sub>3,5</sub> <sup>O<sub>2</sub></sup> [€/kmol]	0.001231	€ <sub>2,8</sub> <sup>O<sub>2</sub></sup> [€/kmol]	0.001119
€ <sup>Ar</sup> [€/kmol]	0.002026	€ <sub>energy</sub> [€/kmol]	0.075

The revenues coming from the recovered energy are not discounted (5). It is reasonable under the assumption of an inflation factor completely balanced by the increase of energy price. The results obtained

using data and formulas and the PBT are reported in Table 4. Economic analysis proves that the investment is convenient since NPV is positive. PBT is about a quarter of the expected life of the investment, but taking into account that the energy market is still growing, this investment seems to be quite appealing. Similarly, intensifications presented can be exploited (Klemeš et al., 2010) whenever the energy supply chain (Čuček et al., 2010) and the rationalization of the regional/national energy consumption (Lam et al., 2010a, b) are the targets.

Table 4: Results

TC [€]	1088271	$\Delta R_{O_2}$ [€/y]	482.11
$\Delta R_{Ar}$ [€/y]	11.47	$R_{energy}$ [€/y]	193141
<b>NPV [€]</b>	<b>1670133</b>	<b>PBT [y]</b>	<b>5.62</b>

## 5. Conclusions

Although air separation units are intended as well-intensified processes for the very tight energy saving policies that usually adopt, they can be further optimized in terms of energy consumptions and sustainability by means of appropriate revamping. Specifically, the modifications to upgrade the oxygen purity using nitrogen-argon profile decoupling, to reuse the argon vent, and to generate power expanding oxygen stream have been proven to be effective.

## References

- Čuček, L., Lam, H.L., Klemeš, J.J., Varbanov, P.S., Kravanja, Z., 2010. Synthesis of regional networks for the supply of energy and bioproducts. *Clean Technologies and Environmental Policy*, 12, 635-645.
- D'Isanto, M., Manenti, F., Lima, N.M.N., Zuniga Linan, L., 2011. Corporate Production Planning for Industrial Gas Supply Chains under Low-Demand Conditions. *Computer Aided Chemical Engineering*, 29, 965-969.
- Huang, R., Zavala, V.M., Biegler, L.T., 2009. Advanced step nonlinear model predictive control for air separation units. *Journal of Process Control*, 19, 678-685.
- Jiang, L., Biegler, L.T., Fox, V.G., 2003. Simulation and optimization of pressure-swing adsorption systems for air separation. *AIChE Journal*, 49, 1140-1157.
- Klemeš, J.J., Varbanov, P.S., Pierucci, S., Huisingh, D., 2010. Minimising emissions and energy wastage by improved industrial processes and integration of renewable energy. *Journal of Cleaner Production*, 18, 843-847.
- Lam, H.L., Varbanov, P., Klemeš, J., 2010a. Minimising carbon footprint of regional biomass supply chains. *Resources, Conservation and Recycling*, 54, 303-309.
- Lam, H.L., Varbanov, P.S., Klemeš, J.J., 2010b. Optimisation of regional energy supply chains utilising renewables: P-graph approach. *Computers and Chemical Engineering*, 34, 782-792.
- Manenti, F., Bozzano, G., D'Isanto, M., Lima, N.M.N., Zuniga Linan, L., 2013. Raising the Decision-Making Level to Improve the Enterprise-Wide Production Flexibility. *AIChE Journal*, DOI 10.1002/aic.
- Marangoni C., Meneguelo A.P., Teleken J.G., Parisotto I.G.B., Werle L.O., Machado R.A.F., Carvalho Dos Santos M., Gomes A.O., Medina L.C., 2011. New Configuration of a Distillation Process with Reduced Dimensions, *Chemical Engineering Transactions*, 24, 799-804,
- Park, M., Park, S., Mele, F.D., Grossmann, I.E., 2006. Modeling of purchase and sales contracts in supply chain optimization. *Industrial & Engineering Chemistry Research*, 45, 5013-5026.
- Simsci-Esscor, 2002. PRO/II, User Guide. Lake Forest, CA, USA.
- Smith, A.R., Klosek, J., 2001. A Review of Air Separation Technologies and their Integration with Energy Conversion Processes. *Fuel Process. Technol.*, 70 (2), 115.
- Ydstie, B.E., 2004. Distributed Decision Making in Complex Organizations: the Adaptive Enterprise. *Computers and Chemical Engineering*, 29, 11-27.
- Zhu, G.Y., Henson, M.A., Megan, L., 2001. Low-order dynamic modeling of cryogenic distillation columns based on nonlinear wave phenomenon. *Separation and Purification Technology*, 24, 467-487.