SOME ASPECTS CONCERNING ARGON PRODUCTION BY CRYOGENIC AIR SEPARATION

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ABSTRACT

Argon is obtained in an air separation unit by cryogenic rectification, like a by-product. Crude argon is obtained in a side column, which is direct linked to the low pressure column. Despite the fact that argon concentration in air processing is only 0.93 %, it is shown that in a specific location through low pressure column, its concentration increase to about 16 %. It is very important the flow extracted from low pressure column end sent to the crude argon column be located there and, more important, the argon "belly" be maintened in the same position. Because this, the low pressure column is the key component in order to obtain high recovery and purity not only for the argon product but, at the same time, for high purity nitrogen and oxygen products.

Keywords*: air separation, cryogenic rectification, air components, concentration distribution*

1. INTRODUCTION

Argon has become one of the most valuable gases, especially after 1970, when there was a great interest in special steel production. At the same time, argon is used in medicine, welding technology, electronics and lighting. Argon can be produced from air (its concentration in atmospheric air is 0.93 % in volume) or in ammonia synthesis technology [Smith, A.R., Klosek, J., 2001]. Large quantities and high purity of argon can be obtained just from cryogenic air distillation. The most abundant components in dry atmospheric air are nitrogen, oxygen and argon. The typical distillation section of a cryogenic air separation plant contains a double column (producing nitrogen and oxygen products, both in vapor and liquid state) and a side crude argon column. The crude argon product is then purified. In old plants, argon purifying is produced in a DEOXO system, where oxygen is removed in a catalytic process, using hydrogen. In air plant constructed after 1990, argon is obtained in a pure argon column, by using a structured column.

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2. PROCESS OVERVIEW

The separation process presented in this paper produces gaseous nitrogen, oxygen and argon products. Part of the oxygen is also produced as liquid. The flow sheet of the process is presented in figure 1. The oxygen and the nitrogen are separated in a double distillation column. This column consists of two separate columns which are located one above the other. The bottom column (HP column) operates at higher pressure and a condenser is located at the top of the column and the upper column (LP column) operates at a lower pressure; a reboiler is located at the bottom of the column. The two columns are thermally integrated, the condenser and the reboiler being coupled in a single heat exchanger. The HP column bottom product, an oxygen enriched liquid is introduced in the LP column as feed and the HP column top product, which is liquid nitrogen, is introduced at the top of the LP column, ensuring the reflux in this column. An argon enriched flow is extracted from the LP column and it is introduced at the bottom of the crude argon column. A condenser is placed at the top of this column. The flux which rises in the crude argon column contains argon and oxygen. In the top condenser, oxygen is condensed and ensures the reflux in the crude argon column. This condensation is possible by heat exchange between argon column flux and oxygen enriched liquid extracted from the bottom of the HP column. The remaining vapor from the flux in the crude argon column are extracted, and the reflux, which is mostly liquid oxygen, is extracted from the bottom of the crude argon column end introduced in the LP column, bellow the argon column feed extraction.

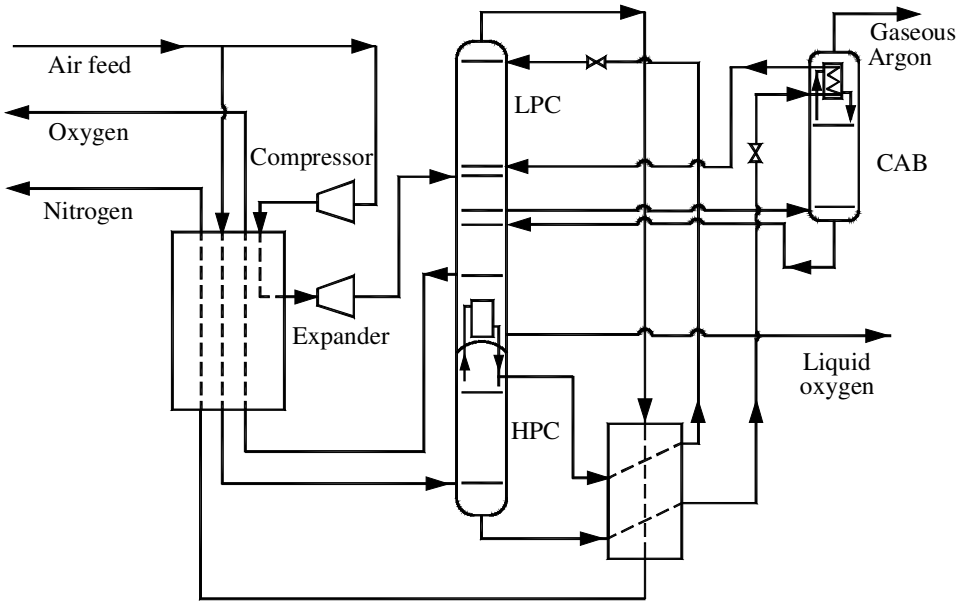

Figure 1. Typical block flow diagram for an air separation unit

The process is simulated using PRO II software [Lee, B., Kesler, M., 1975]. The challenge in process simulation is to solve a thermal and substance integrated process and the air must be treated like a ternary mixture (oxygen, nitrogen and

argon). This is extremely important when the low pressure column is simulated. Another characteristic of this column is unsteady regime during operation. Thermodynamic calculation of this process cannot be underestimated, because the separation product purities is high and the temperature differences are only a few degree. The equation of state Soave-Redlich-Kwong is used for equilibrium, enthalpy and vapor density calculation. It is important to use binary interaction parameters obtained near the boiling temperature of components at a specific pressure range for each pair, in order to obtain an accurate simulation model. These interaction parameters are obtained either from data base of the companies which operate this kind of plants or through regressing experimental vapor-liquid equilibrium data.

The basic model for a distillation column is stage-by-stage equilibrium model. From energy equilibrium inside of column, the following equations are obtained [Harmens, A. 1970]:

For the high and low pressure column:

$$V_{j+1}\cdot H_{j+1}^{V}+L_{j-1}\cdot H_{j-1}^{L}+F_j^{V}\cdot H_j^{FV}+F_j^{L}\cdot H_j^{FL}-\left(V_j+S_j^{V}\right)\cdot H_j^{V}-\left(L_j+S_j^{L}\right)\cdot H_j^{L}-Q_j=0 \quad (1)$$
$$1\le j\le n-1,\quad n+2\le j\le n+m$$

For the crude argon column:

$$V_{j+1}\cdot H_{j+1}^{V}+L_{j-1}\cdot H_{j-1}^{L}+F_j^{V}\cdot H_j^{FV}+F_j^{L}\cdot H_j^{FL}-V_j\cdot H_j^{V}-L_j\cdot H_j^{L}-Q_j=0 \quad (2)$$
$$1\le j\le n-1$$

$$L_{j-1}\cdot H_{j-1}^{L}+F_j^{V}\cdot H_j^{FV}+F_j^{L}\cdot H_j^{FL}-\left(V_j+S_j^{V}\right)\cdot H_j^{V}-\left(L_j+S_j^{L}\right)\cdot H_j^{L}-Q_j=0 \quad (3)$$
$$j=n$$

F_j^{V} and F_j^{L} are the gas and the flow that enters on stage j respectively.

S_j^{V} respectively S_j^{L} are gas and liquid side withdraw out of j th stage, and Q_j is the heat input on j th stage.

According to component material balance, the following equations are derived:

$$V_{j+1}\cdot y_{i,j+1}+L_{j-1}\cdot x_{i,j-1}+F_j^{V}\cdot z_{i,j}^{V}+F_j^{L}\cdot z_{i,j}^{L}-\left(V_j+S_j^{V}\right)\cdot y_{i,j}-\left(L_j+S_j^{L}\right)\cdot x_{i,j}=0 \quad (4)$$
$$i=1,2,3,\quad 2\le j\le n-1$$

$$V_{j+1}\cdot y_{i,j+1}+F_j^{V}\cdot z_{i,j}^{V}+F_j^{L}\cdot z_{i,j}^{L}-\left(V_j+S_j^{V}\right)\cdot y_{i,j}-\left(L_j+S_j^{L}\right)\cdot x_{i,j}=0 \quad (5)$$
$$i=1,2,3,\quad j=1$$

$$L_{j-1}\cdot x_{i,j-1}+F_j^{V}\cdot z_{i,j}^{V}+F_j^{L}\cdot z_{i,j}^{L}-\left(V_j+S_j^{V}\right)\cdot y_{i,j}-\left(L_j+S_j^{L}\right)\cdot x_{i,j}=0 \quad (6)$$
$$i=1,2,3,\quad j=n$$

where $x_{i,j}$, $y_{i,j}$ and $z_{i,j}$ mean mole fraction of liquid, vapor and feed flow of i component on j th stage.

From principle of mole fraction, the following equations are derived:

$$\sum_{i=1}^{C} x_{i,j} = 1 \text{ and } \sum_{i=1}^{C} y_{i,j} = 1 \tag{7}$$

For high and low pressure column, $C = n + m$, and for crud argon column $C = n$.

According to the vapor-liquid equilibrium relationships, the vapor composition is obtained:

$$\begin{cases} y_{i,j} = K_{i,j} \cdot x_{i,j} \\ K_{i,j} = r_{i,j} \cdot F_{i,j} \end{cases} \tag{8}$$

$$\begin{cases} \log r_1 = \left(a_1 \cdot x_3^2 + b_1 \cdot x_2^2 + c_1 \cdot x_3 \cdot x_2\right) / T \\ \log r_2 = \left(a_2 \cdot x_1^2 + b_1 \cdot x_3^2 + c_1 \cdot x_3 \cdot x_1\right) / T \\ \log r_3 = \left(a_3 \cdot x_2^2 + b_1 \cdot x_1^2 + c_1 \cdot x_1 \cdot x_2\right) / T \end{cases} \tag{9}$$

$$\log F_i = \left(h_i^1 + \frac{h_i^2}{\sqrt{p}} + h_i^3 \sqrt{p} + h_i^4 p \right) - \frac{h_i^5 + h_i^6 p + h_i^7 p^2}{T} + h_i^8 T \tag{10}$$

where $K_{i,j} = \dfrac{y_i}{x_i}$ is the equilibrium vaporization ratio, y_i and x_i represent molar fractions of i component in vapor phase, respectively liquid phase, r_i is the fugacity coefficient of ith component on jth stage, while $F_{i,j}$ is experience formula.

For air and its components (oxygen, nitrogen and argon) Peng-Robinson equation of state is applicable:

$$p = \frac{RT}{V - b} - \frac{a}{V^2 + 3bV - 2b^2} \tag{11}$$

where:

$$a = \left(K - L\tau + M\tau^2 - N\tau^3\right) \cdot R_2 T_c^2 / p \tag{12}$$

$$b = 0.070721 \cdot RT_c / p_c \tag{13}$$

$$\tau = 0.01T \tag{14}$$

The enthalpies, entropies and concentrations are calculated with the following relationship:

$$H = H^* - RT(1 - Z) - \xi\left(a - T\frac{da}{dT}\right) / b \tag{15}$$

$$H^* = b_{10} + b_{11}T + b_{12}T^2 + b_{13}T^3 + b_{14}T^4 \tag{16}$$

$$S = S^* - R \ln \frac{RT}{V - b} + \xi \frac{da}{dT} / b \tag{17}$$

$$S^* = b_{11} \ln T + 2b_{12}T + 1.5b_{13}T^2 + \frac{4}{3}b_{14}T^3 + c_0 \tag{18}$$

$$\xi = 0.242536 \cdot \ln\left[\left((V + 3.561553b)/(V - 0.561553b)\right)\right] \tag{19}$$

3. CONCENTRATION PROFILE IN DISTILLATION COLUMNS

All the thermodynamic data result from the simulation process. One of the most important is the concentration profile of the component in distillation column. The concentration profile in high pressure column is presented in figure 2.

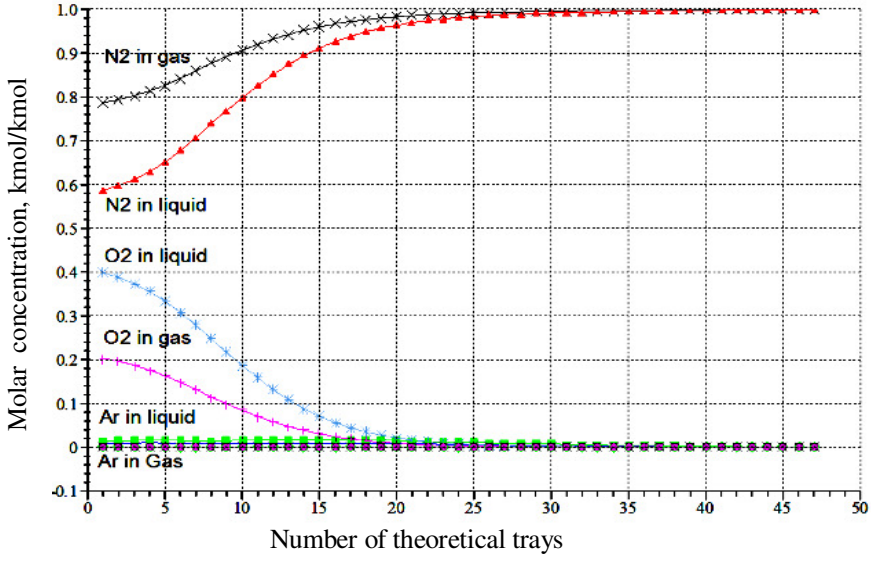

Figure 2. Components distribution in the high pressure column

We can see that there is no variation of argon concentration in this column. This is because the pressure column is about 6 bar. The relative volatility between argon and oxygen is slightly greater than 1 and there is no rectification process.

The concentration profile in low pressure column is presented in figure 3.

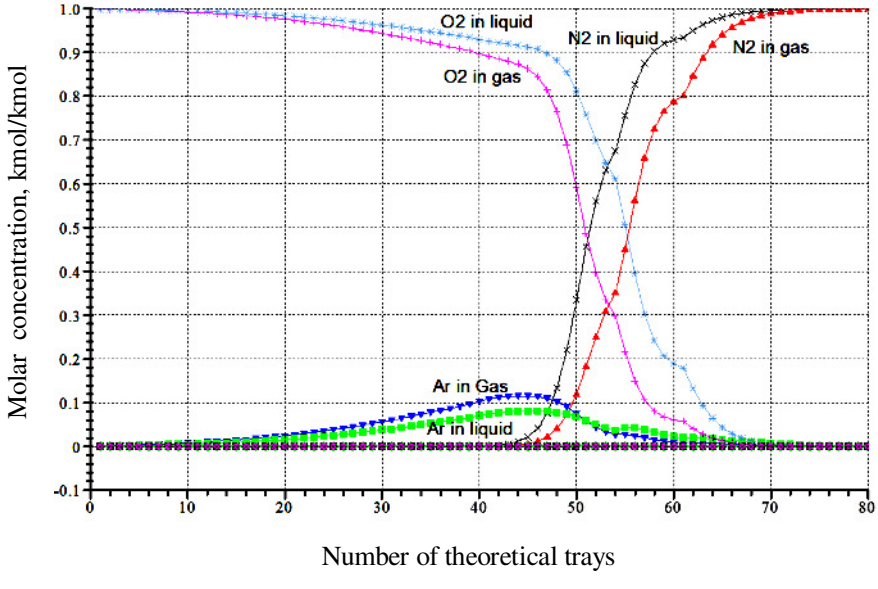

Figure 3. Components distribution in the high pressure column

Despite the fact that the argon concentration in atmospheric air is 0.93 %, in the LP column the argon concentration can reach 16%. That because the boiling point of argon (87.2 K) is between the nitrogen point (77.3 K) and the oxygen point (90.2 K). There is an "argon belly" in the LP column. To obtain a high recovery rate of argon from processed air, the flow sent to the crude argon column must be located in the "argon belly" area.

The concentration profile in crude argon column is presented in figure 4.

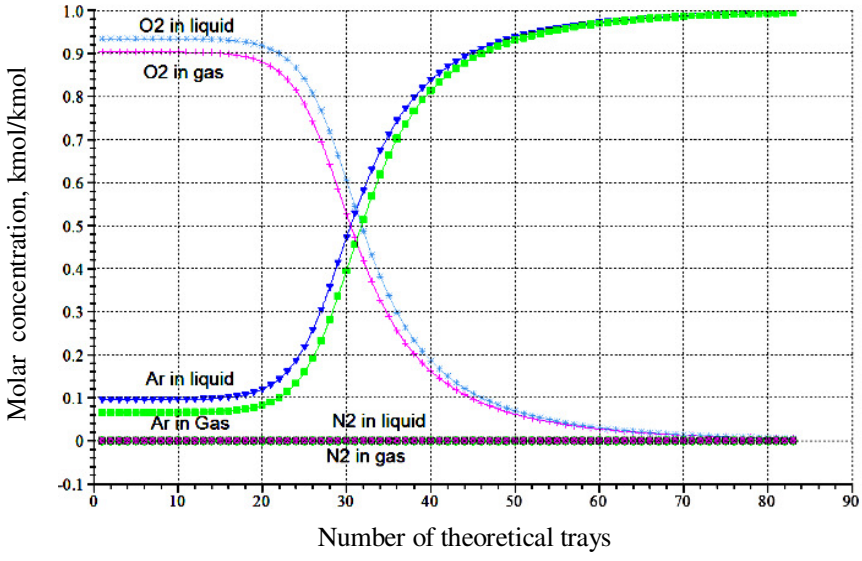

Figure 4. Components distribution in the high pressure column

We can observe that, in this column, the nitrogen concentration variation is very slight. This is because de temperature in the condenser placed at the top of the crude argon column is lower than the nitrogen boiling temperature. In that situation, nitrogen will remain in the vapor phase and it will be extracted in crude argon product.

4. DISCUSSION

Keeping in mind the component concentrations in each distillation column, the most significant variation of argon concentration is in the LP column.

If we arrange in some way the concentration profile in this column, a significant component distribution results in this column (figure 5). Argon in incoming air must be evacuated by argon production, liquid oxygen product and waste nitrogen [Manenti, F, 2013].

In figure 5a, the argon transition point is set at 90% oxygen content. In this situation, argon concentration is lower than the maximum value, but at the same time nitrogen concentration is minimum. Thus, we can avoid large nitrogen quantities in the crude argon column. If we set the transition point at 92% oxygen (figure 5b), the concentration profile goes up and the argon content in waste nitrogen will increase. To keep the argon mass balance, argon production must be decreased.

Supposing that argon production has been increased to theoretical value (figure 5c), in order to keep argon mass balance, the argon in the waste nitrogen must be decreased. For 92% oxygen concentration, the argon belly must be narrower; it is exhausted and allows nitrogen to go down to the argon transition point.

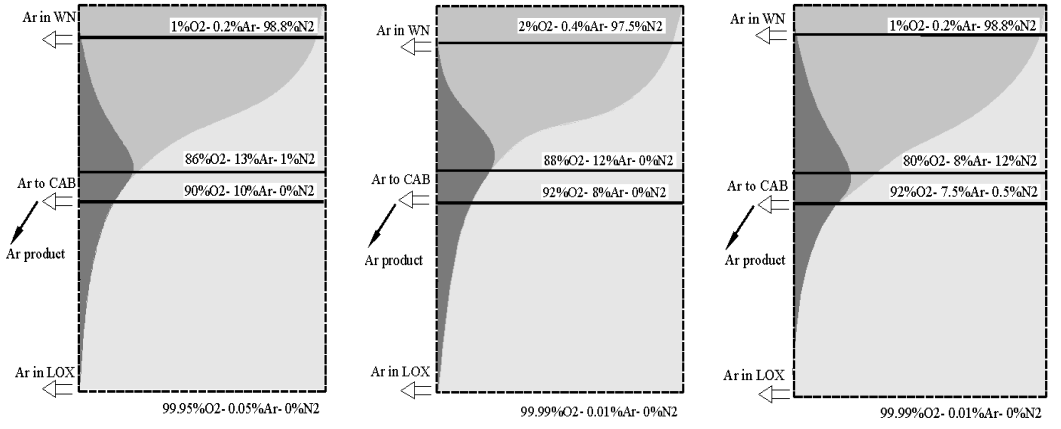

Figure 5. Argon belly position for different operating regime: (a)-normal operating; (b)-92% oxygen concentration; (c)-nitrogen breakthrough

The argon transition should be regulated by argon, not by nitrogen. Argon reflux can regulate argon transition with much lower nitrogen breakthrough potential. The lower argon reflux will involve lower argon transition flow. At the same time, lower argon reflux involves higher liquid oxygen and less liquid nitrogen production. Generally, nitrogen in argon transition is not a problem, if argon transition is below 89% oxygen content, but this will involve missing the argon belly by argon misbalance. Nitrogen can be pushed up by argon, which is generally better that by liquid oxygen. If argon reflux decreases, the argon transition must decrease as well, otherwise argon will be pushed to waste nitrogen by higher vapor oxygen and it will be lost.

5. CONCLUSION

Key parameters for argon optimization recovery are:

1. Waste nitrogen – higher oxygen purity involves higher argon loss. Variable waste nitrogen means higher argon loss and earlier nitrogen breakthrough.
2. Gaseous oxygen purity – lower oxygen purity means argon high loss.
3. Argon column feed flow/column pressure drop – Too high flow means early nitrogen breakthrough, too low has the effect of not achieving the desired argon purity.
4. Argon column/ low pressure column stability is enhanced when full argon is recovered.
5. To avoid any disturbance, the entire argon column/low pressure column must be in the right place.

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