Optimization of the air separation process in single stage cryogenic units

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Abstract — **The industrial use of cryogenic air separation units started more than 130 years ago. Cryogenic air separation units produce oxygen, pure nitrogen and argon in liquid and/or gaseous state. Different configurations of these cryogenic plants lead to different quantities of gas and liquid products. In addition, product purity is also affected by the proposed scheme. As a result, the paper analyzes different variants of installations for the separation of binary gas mixtures based on the Linde process. By comparing energy indices and constructive considerations, the separation plant with external air pre-cooling and the use of a single-stage separation column is chosen. Finally, a study is carried out on the processes in the separation column and a calculation of the minimum mechanical work of separation. The real air consumption curve will also be built, with the help of which we shall determine what quantities of O_2 and N_2 are obtained by air separation at a specific consumption.**

Keywords - air separation unit, energetic analysis, rectification column, optimization

I. INTRODUCTION

Cryogenic air separation is the dominant process for supplying significant quantities of high-purity industrial gases such as oxygen, nitrogen, and argon that serve the steel, chemical, petroleum, and aeronautical industries [1]. The process of separating a mixture takes place at the lowered temperature at which it liquefies; for example, the air separation process takes place at temperatures of 95 - 78K.

Air is a simple physical mixture formed of nitrogen (78%), oxygen (21%) and argon (0,9%), in which these gases are not chemically combined. These gases mix spontaneously, without external energy consumption, but the subsequent separation of the mixture into its component parts cannot take place spontaneously and requires energy consumption. The separation of air into oxygen and nitrogen, its fractionation to a gaseous state is very difficult to achieve in practice, because the oxygen and nitrogen particles form a very intimate mixture. It is much easier to separate the air in a liquid state. To obtain low and very low temperatures, so to obtain deep cold, the liquefaction and separation of gases is necessary, the following general methods are usually used: liquid vaporization using a four-stage cascade installation; the use of the Joule-Thomson throttling effect; the polytropic expansion of the gas in the expander, with the production of mechanical work [2]. In 1902, Linde designed the first cryogenic distillation column to separate O_2 from air. The single-column design

recovered only 67% of the O_2 from the compressed air stream and was therefore inefficient [3]. Since the liquid reflux of a single column is liquid air, the distillate vapor at the top of the column contains about 7% O_2, which results in a low O_2 recovery rate for a single column [3], [4]. In 1910, Linde modified the process by incorporating air pre-separation in another high-pressure column. The new dual-column ASU produced N_2 and O_2 products simultaneously and achieved a very high O_2 recovery rate, which revolutionized the industry and is still the forerunner of modern air oxygen plants [3], [4].

II. DESCRIPTION OF THE CRYOGENIC CYCLES FOR LIQUEFACTION

In a cryogenic air separation unit (ASU), air is first compressed to a high pressure and then liquefied at a very low temperature. The liquefied air is separated into high-purity oxygen, nitrogen and argon through a series of distillation columns and other equipment. With the exception of argon, which is usually liquid, the final products can be either in gas phase or liquid phase, depending on the type of use and process design.

Below, we will compare three liquefaction installations based on the Linde process, aiming to obtain liquid oxygen: the Simple Linde-Hampson, Dual pressure Linde and precooled Linde (Fig. 1). A comparative study of the three liquefaction cycles is performed using the Engineering Equation Solver (EES) software [5]. The thermal calculation of the liquefaction installations is made and the liquefaction coefficient, the specific refrigeration power, the specific mechanical work consumed by the compressor, the refrigeration efficiency of the installations and the specific energy consumption are determined.
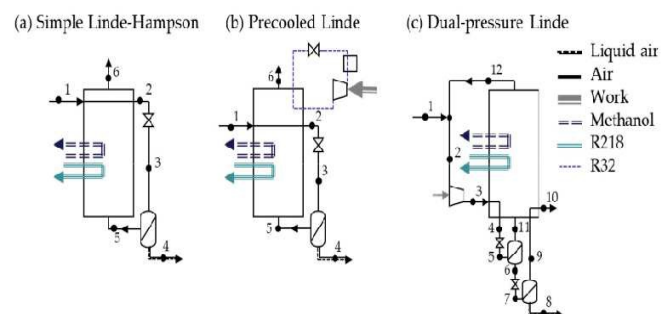

Fig. 1. Linde-based air liquefaction processes [6].
(a) – Simple Linde-Hampson cycle; (b) – Precooled Linde;
(c) – Dual-pressure Linde cycle

The plants have the following operating conditions:

-air flow: $\dot{m}=2000\ kg/h$

- suction pressure in the compressor p_1=1 bar
- aspirated air temperature: T_1=300 K;
- purity of produced oxygen: 99.7%
- purity of produced nitrogen: 96%
- pressure at the end of the compression: p_2=200 bar;
- heat gains due to incomplete heat recovery: q_n=7 kJ/kg
- heat gains due to heat flow from outside: q_i=6 kJ/kg
- η_{iz}=0,6 (izentropically efficiency at compressor)

Mathematical modeling:

Fraction y of obtained liquefied air is determined by writing the thermal balance in relation (1):

$$y = \frac{h_1 - h_2 - q_n - q_i'}{h_1 - h_0 - q_n} \qquad (1)$$

where h [kJ/kg] is specific enthalpy.

The real specific cooling power of the cycle:

$$q_{0,r} = y \cdot q_0 = y \cdot (h_1 - h_0) \qquad (2)$$

The specific mechanical work consumed by the compressor:

$$l_c = \frac{1}{\eta_{iz} \cdot \eta_{mcp}} \cdot R \cdot T \cdot \ln\left(\frac{p_2}{p_1}\right) \qquad (3)$$

where R=287J/kgK

Refrigeration efficiency of the installation:

$$\varepsilon_f = \frac{q_{0,r}}{|l|} \qquad (4)$$

Specific energy consumption for producing 1 kg of liquid air:

$$K = \frac{|l_{ef}|}{y} \ [kWh/kg\ liquid] \qquad (5)$$

Following the thermal calculation, the results shown in table 1 were obtained.

TABLE I.   THE ENERGY CHARACTERISTICS

Energy characteristics	Simple Linde-Hampson cycle	Precooled Linde cycle	Linde Dual-Pressure cycle
Liquefaction coefficient y [kg liquid/kg compressed air]	0.04895	0.155067	0.04032
Specific cooling power $q_{o,r}$ [kJ/kg]	21.09	55.076	17.37
Mechanical work consumed l [kJ/kg compressed air]	767.912	796.016	373,066
Refrigerating efficiency	0.04577	0.069	0.0467
Specific energy consumption K [kWh/kg liquid]	4.358	1,426	2.56

Comparing these values, it is found that the introduction of double throttling in the installation based on the Linde

cycle determines the improvement of most of the characteristics taken into account: the decrease of the specific mechanical work consumed for compression, as well as the decrease of the specific energy consumption. The same thing happens in the case of the installation based on the Linde cycle with air pre-cooling, where the improvement of two characteristics: the liquefaction coefficient and the specific energy consumption, determines the increase of the specific mechanical work consumed for compression. Due to these reasons, it is concluded that the optimal option is the installation based on the Linde cycle with air pre-cooling.

Precooled Linde plant includes the following devices according to figure 2 and figure 3: a four-stage air compressor in which the air is compressed from p_1=1 bar to the pressure p_2=200 bar; R – final cooler of compressed air, which works with water; a heat exchanger (S), working with ammonia, in which compressed air cooling takes place; SC_1 and SC_2 – countercurrent heat exchangers, in which the heat transfer takes place from the compressed air to the cold gas vapors coming from the separation column; VL_1 throttling valve in which air pressure decreases from p_2 to p_1 and the simple separation/rectification column (Cs) in which air is separated into its components. The separation column has two zones: the rectification zone represented by the upper portion of the rectification column and the exhaustion zone represented by the lower portion of the rectification column. The column with simple rectification can be used for the complete extraction of oxygen if in its upper section it is introduced together with liquid air and liquid nitrogen (state 8), obtained in a separate refrigeration circuit. The cooled air with state 5 is introduced at the middle of the height of the separation column, and the circulating nitrogen with state 9 is introduced into the condenser and then into the upper part of the column. In the separation column, the fraction *y* kg of liquid oxygen is separated from each kg of wet vapors produced by lamination. By condensing this quantity, the heat required to vaporize the quantity *(1-y)* kg of nitrogen vapor is obtained, which is then isobarically heated in the countercurrent heat exchangers SC_1 and SC_2, theoretically up to the states 1'' (at the exit from SC2) and 1 (at the exit from SC_1), but in reality up to states 1''' and 1'' respectively, due to the incomplete heat recovery (q_n) [7].
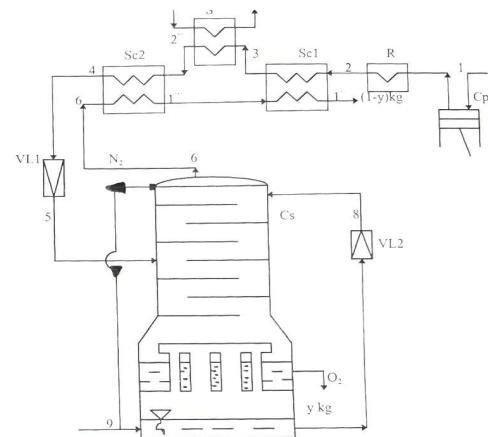

Fig. 2. Precooled Linde's single column [7]

The concentration of the vapors produced in the column depends on the concentration of circulating nitrogen and is close to it. During the start-up period, the column cools

down to air liquefaction temperatures, after which the liquid accumulates in the tank and on the column plates. In the rectification column, the process of countercurrent flow of the vapor phase and the liquid phase takes place, which influence each other through the contact surfaces .
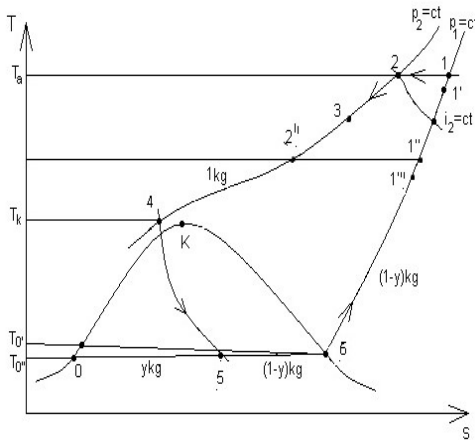

Fig. 3.   T-s diagram of the cycle [7]

III.   SEPARATION COLUMN CALCULATION

Minimum separation mechanical work

The separation of a gas mixture into its pure components can only be achieved with external energy consumption, even if the separation is done through irreversible processes .

$$L_{\min} = T_o \cdot \Delta s_{sep} \left[\frac{J}{kmol} \right] \qquad (6)$$

$$\Delta s_{sep} = -R_M \cdot \left(y_1 \ln \frac{1}{y_1} + y_2 \ln \frac{1}{y_2} \right) \qquad (7)$$

As $y_2 = 1 - y_1$ it results that:

$$\Delta s_{sep} = R_M \cdot \left(y_1 \ln y_1 + (1 - y_1) \ln(1 - y_1) \right) \left[\frac{J}{kmol \cdot K} \right] \quad (8)$$

For a binary mixture of gases (M_o, y_o): with a main component (P, y_P) and a secondary component (W, y_w), the entropy variation in the separation process will be [8]:

$$\Delta s_{sep} = M_o \cdot \Delta s_o - P \cdot \Delta s - W \cdot \Delta s_w \left[\frac{J}{kmol \cdot K} \right] \qquad (9)$$

where:

$$\Delta s_P = R_M \cdot \left(y_P \ln y_P + (1 - y_P) \ln(1 - y_P) \right) \qquad (10)$$

$$\Delta s_w = R_M \cdot \left(y_w \ln y_w + (1 - y_w) \ln(1 - y_w) \right) \qquad (11)$$

$$\Delta s_o = R_M \cdot \left(y_o \ln y_o + (1 - y_o) \ln(1 - y_o) \right) \qquad (12)$$

Quantities of main and secondary products are shown in Table II.

TABLE II

Concentration [%]	W[kmol]	P[kmol]	nc	ne
98	0.808	0.198	16	30
96	0.822	0.178	12	27
94	0.84	0.16	8	27
92	0.858	0.142	8	24
90	0.877	0.123	6	20

Table III was made in order to calculate the minimum separation mechanical work:

TABLE III.

Con-cent	Δs_0 [J/kmolK]	Δs_P [J/kmolK]	Δs_W	Δs_{sep}	L_{min} [J/kmol]
98	-4273.19	-169.802	-815.127	-3582.57	-1075000
96	-4273.19	-169.802	-1396.34	-3095.18	-928600
94	-4273.19	-169.802	-1887.08	-2660.88	-798200
92	-4273.19	-169.802	-2317.77	-2260.42	-678128
90	-4273.19	-169.802	-2703.84	-1881.92	-564600

The number of trays on the concentration and exhaust areas of column are shown in Table II and figure 4 [9], [10]:
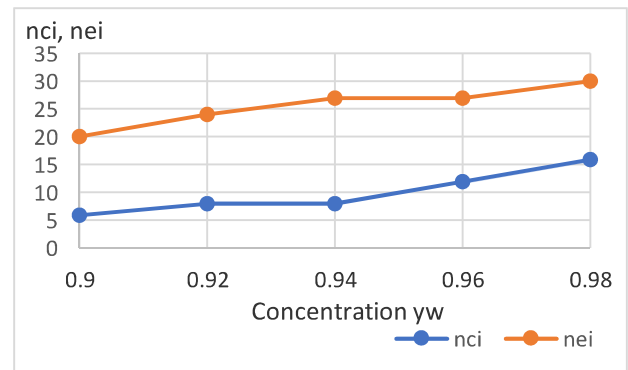

Fig. 4.   No. of trays against/vs concentration y_w

One can notice an increase of the number of trays when the secondary product concentration increases.

Regarding the consumption of separation mechanical work, one can notice its increase when the secondary product concentration increases (figure 5).
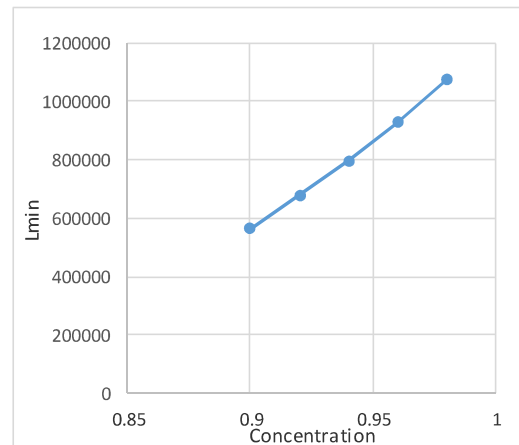

Fig. 5.   The graph of the function L_min against/vs concentration y_w.

IV.   DESIGNING THE REAL AIR CONSUMPTION CURVE

Plotting this curve allows us to rapidly determine what quantities of O_2 and N_2 are obtained by air separation at a specific consumption. The real air consumption (c_{real}) curve is designed solving a series of mass/volume balance equation, as many times as how many points we need in order plot the curve to. For example, we shall plot the curve using five points.
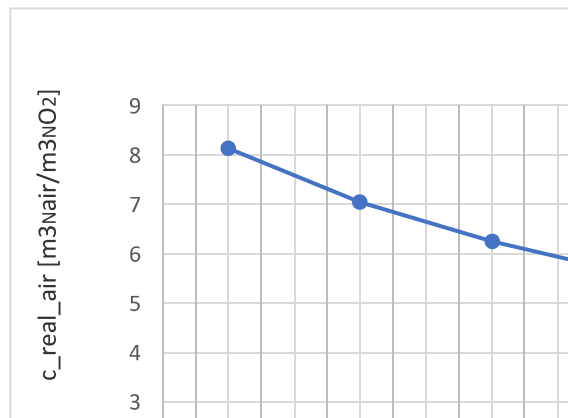
Fig. 6.   The graph of the function $c_{real} = f(y_w)$.

V. CONCLUSIONS

In the work presented in this paper, the analysis of a Linde installation for oxygen production with a single throttling and with air pre cooling was made.

Oxygen with a purity of 99.7% is produced and, as a secondary product, a gaseous mixture containing 97% N_2 and 3% O_2. In the research carried out, the concentration of nitrogen (by-product) was increased in the range between 90% and 99% and the influence of such an increase on the operation of the distillation column was analyzed. Following the calculations, it can be stated that the air mass flow rate to the cryogenic installation decreases with the increase in the concentration of the secondary product, which translates into a lower energy intensity of the distillation process in the cryogenic module.

Additional research, including exergy and economic analyses, will be conducted by the authors.

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