MODELING OXYGEN PRODUCTION VIA CRYOGENIC AIR SEPARATION

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Abstract

Industrial-scale oxygen production is vital for many industrial branches, where it serves for energy efficient production of materials, as gasification agent or to produce chemicals. Current technologies exhibit a rather large specific power consumption, exceeding 150 kWh per ton of pure oxygen. With several of them being mature for decades, while others being still in development, possibilities for further energy consumption decrease should be exploited, to make the oxygen production via air separation more sustainable. With this long-term goal a model Cryogenic Air Separation Unit (ASU) is considered as a case study. Its performance as a stand-alone plant is modeled and verified. Possible synergies resulting from its incorporation in a refinery are highlighted, together with the idea of using the oxygen for heavy residues gasification, while nitrogen being supplied to the refinery for inertization purposes. Deeper energy integration with the refinery energy management could deliver additional power consumption reduction. The presented case study and its result contribute to sustainable industrial-scale oxygen production goal, while retaining a favorable production economy and exploiting the potential of carbon footprint reduction.

Introduction

Oxygen is the second most used gas in industry. It is used in food, chemical, oil industry, pharmacy, and others, with varying purity, state, and quantity requirements. The global oxygen market was worth \$37.93 billion in 2019. It is expected to grow at a compound annual growth rate (CAGR) of 11% and reach \$59.17 billion by 2023. In 2019, Future Market Insights (FMI) reported that overall sales of industrial oxygen reached approximately 380 million tons in 2018 [1].

To separate individual components of air, most air must be liquified. Gas can only be liquified at temperatures and pressures below its critical point; critical point of air is at T_c = 132.5 K and pressure P_c = 37.7 bar. Two liquefaction cycles are known, namely Linde and Kapica cycle.

There are two different ways of producing oxygen: non-cryogenic and cryogenic production route. Non-cryogenic separation methods include membrane processes and pressure swing adsorption, both operated at ambient temperature.

Study objectives

Several goals are defined in this work.

- Design a process scheme based on literature research
- Determination of the required theoretical stages
- Enthalpy and material balance of system
- Calculation of the duty of the heat exchangers, expander, condenser/vaporiser

Air Separation Unit (ASU) description

Cryogenic separation method is based on different boiling points of mixture components. This method was invented by Carl von Linde and was first used in industry in the 20th century. Distillation columns used for the separation are placed in "cold boxes" where the temperature is very low. Thermodynamic minimal work of oxygen separation from air is equal to 53.1 kWh per ton of oxygen. In 2015, the most efficient ASU exceeded the minimum energy three times [2].

The designed scheme can be divided into three sections. The first section provides air compression and water removal. In this work, air is considered as a three-component mixture composed of nitrogen, oxygen, and water vapor. Due to the process layout, it has to be compressed to the pressure of 6 bar which is done by two-stage compression, with an intercooler and final cooler, both serving as partial condensers of water vapor at the same time. The rest of the water vapor is removed in an adsorber. Air leaving the adsorber is divided into two streams, in a ratio to be estimated.

Both streams enter the main heat exchanger, where they are pre-cooled by process effluents. One fraction of air proceeds through the expander, where it expands to the pressure of 1.5 bar and flows to the upper column. The second stream flows directly to the lower column.

The third section, includes a separation column and a secondary heat exchanger. The column consists of a low-pressure column (LPC) which is the upper column, and a high-pressure column (HPC). Condenser of nitrogen vapors in HPC serves as the LPC reboiler. A part of the condensed nitrogen is used as a reflux for HPC. The main product is oxygen, obtained in the lower part of LPC. The secondary heat exchanger serves as a pre-cooler for streams that serve as refluxes for LPC.

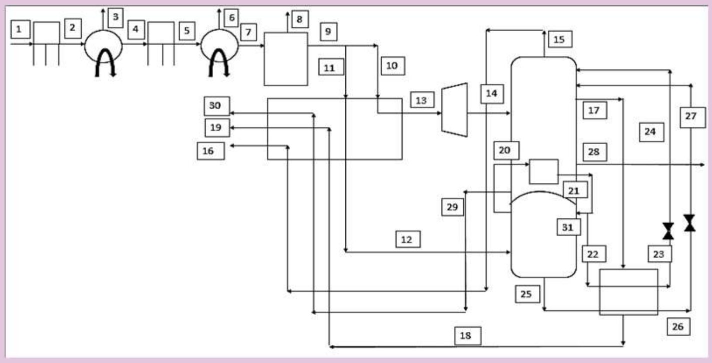

Figure 1: Designed scheme of cryogenic air separation

Model assumptions and equations

Real equilibrium data are obtained by the Peng-Robinson thermodynamic model in AspenPlus software. X-y equilibrium diagrams were constructed, and the number of theoretical stages required was determined using the McCabe-Thiele method.

The first section involving compression and removal of water vapor is calculated by a set of equations. Mass flow of dry air, $\dot{m}_G$, is calculated by equation (1)

$$\dot{m}_G = \frac{\dot{m}_1}{1+\overline{Y_1}} \quad (1)$$

where, $\dot{m}_1$ is the mass flow of air (kg.h^{-1}), and $\overline{Y_1}$ is the relative mass fraction of water vapor (kg.kg^{-1}). Since air is compressed by two-stage compression, it is necessary to estimate the optimal pressure ratio, β, employing equation (2)

$$\beta = \sqrt{\frac{P_{fin}}{P_0}} \quad (2)$$

where, P_0 is the initial pressure (Pa), and P_{fin} is the final pressure (Pa). Compressor power input is calculated by equation (3)

$$P_n = \frac{R \cdot T \cdot \left(\frac{m_G}{M_G} + \frac{m_G \cdot \overline{Y}}{M_{H_2O}}\right) \cdot \frac{n}{n-1} \cdot \left(\beta^{\frac{n-1}{n}} - 1\right)}{\eta_c} \quad (3)$$

where, R is the molar gas constant (8.314 J.mol^{-1}.K^{-1}), T is temperature (K), M_G is the molar mass of dry gas (kg.mol^{-1}), M_{H_2O} is the molar mass of water (kg.mol^{-1}), n is the polytropic coefficient, and η_c is the overall compression efficiency.

Model results and discussion

In this work, mass flow of air entering the first compressor of 30 t.h^{-1} is considered, with the inlet temperature of 300.15 K and the assumed mass fraction of water vapor of 0.0168. The McCabe-Thiele method helps to determine the number of theoretical stages for each part of the column. For HPC it is 4 stages and for LPC it is 6 stages. The calculated mass flow of condensed water vapor (kg.h^{-1}) in each condenser and adsorber is summarized in Table 1. It is assumed that air leaving the adsorber is dry. Mass balance is summarized in Table 2.

Table 1. Balance of water vapor in the studied process

Mass flow $\dot{m}$ (kg.h^{-1})	*Humidity $\overline{Y}$ (kg.kg^{-1})*
$\dot{m}_3$ = 181.4	$\overline{Y_1}$ = 0.01711
$\dot{m}_6$ = 192.60	$\overline{Y_4^{eq}}$ = 0.01096
$\dot{m}_8$ = 130.66	$\overline{Y_7^{eq}}$ = 4.43.10^{-3}

Table 2. Mass balance of the studied process

Stream Nr.	*Mass flow $\dot{m}$ (kg.h^{-1})*	Stream Nr.	*Mass flow $\dot{m}$ (kg.h^{-1})*
10, 13, 14	4,862	22, 23, 24	12,042
11, 12	24,633	25, 26, 27	12,592
15, 16 ($\dot{N}$)	20,097	28 ($\dot{O}$)	100
17, 18, 19 ($\dot{N}$)	3,533	29, 30 ($\dot{O}$)	5,765
20, 21	25,473	31	13,431

Mass flow of produced oxygen gas, $\dot{O}$, is 5,765 kg.h^{-1} with the purity of 95 %. Stream $\dot{N}$ is almost pure nitrogen, which can also be used as inert gas if ASU is integrated in a refinery, or it can be supplied to other consumers.

The power input of both compressors is approximately the same and reaches 953 kW. This leads to specific power consumption for oxygen production of over 325 kWh per ton of oxygen.

Duty of individual heat exchangers and the separation column were also calculated using the enthalpic balance. The duty of the secondary heat exchanger is 192 kW while that of the main heat exchanger is 1,824 kW and that of combined condenser/vaporizer is 1,195 kW. The amount of work produced in the expander is 50 kW. This work can be used in compressors, lowering the net power consumption of compressors, specifically to the value 316 kWh per ton of oxygen.

The calculated reflux ratio, based on the material and enthalpy balance, is 1.1145.

Conclusion

Based on the literature survey and process material and heat balances, a cryogenic air separation unit was designed, yielding 5,765 kg.h^{-1} of oxygen gas with the purity of 95 % vol. The mass ratio of streams 10 and 11 of 0.1974. A literature survey found that for operations of approximately the same size, this ratio was 0.14.

It was demonstrated that the mixture of oxygen and nitrogen does not behave as an ideal mixture; therefore, its modeling as a real mixture was necessary. Using the McCabe-Thiele method for both ideal and real mixture, the theoretical number of stages in HPC and LPC was estimated.

Since the amount of supplied air is 30 t.h^{-1}, which has to be compressed from 1 bar to 6 bar, two-stage compression was assumed with the calculated power input of both compressor stages being approximately the same, 953 kW. The power input of compressors is too high compared with the most efficient air separation units operated nowadays, so further optimization is needed. This is one of the long-term goals. Enthalpy balance of the separation column and heat exchangers provided their heat duties as 192; 1,824; 1,195 for the secondary heat exchanger, the main heat exchanger, the combined condenser/vaporizer, respectively and 50 kW power output of the expander.

Acknowledgement

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