|  |  |
| --- | --- |
| <cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS*** ***VOL. 76, 2019*** | A publication ofaidiclogo_grande |
| The Italian Associationof Chemical EngineeringOnline at www.cetjournal.it |
| Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura PiazzaCopyright © 2019, AIDIC Servizi S.r.l.**ISBN** 978-88-95608-73-0; **ISSN** 2283-9216 |

Analysis of a possible application of a new process for oxygen enriched air production

G. Bozzanoa, D. Previtalia, S. Zanfini , S. Colomboa, F. Manentia, C. Pirolab

a Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Piazza Leonardo da Vinci 32, 20133, Milano, ITALY;

b Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, 20133, Milano, ITALY;

 Corresponding author: giulia.bozzano@polimi.it

A new process for oxygen enriched air (EA) production has been applied to Claus Process. This process is simple and requires few process units. Matlab and Aspen Hysys have been used for simulations and system sizing. The results demonstrate that it could be an alternative to traditional EA processes from an economical point of view.

* 1. Introduction

Nowadays reduction of waste products and by-products, minimization of energy consumption and polluting emissions, exploitation of plants at their full capacity are fundamental. Oxygen enriched air (EA) can solve, in certain applications, both problems related to polluting emission and the increase of the plant efficiencies. Some researches (Baukal, 1998, Hendershot et al., 2010) have demonstrated that a concentration of oxygen in EA slightly above 21% allows significant improvements. Some examples are related to catalyst regeneration in refinery, fluid catalytic cracking (FCC), partial oxidation of sulfur in Claus plants, wastewater treatment, and combustion applications for glass and foundry operations. If air containing 30% oxygen was used in natural gas furnaces, then natural gas savings would be 28% at a burner temperature of 1650 K. The savings increase becomes less pronounced at higher oxygen concentrations; consequently, the main range of interest is 25% to 35% oxygen. The use of oxygen-enriched air also decreases flue gas volume and increases the CO2 concentration, resulting in significant reduction in the cost of CO2 capture from flue gas. From optimization point of view, EA has different impacts considering an existing plant or during the design. In the first ones, the use of EA can increase, with some revamping operations, the plant capacity can be better exploited. In new plants, higher O2 concentration directly influences plant sizing with a relative economic saving for both capital costs (smaller equipment and piping) and for operating costs (smaller pumps, compressors and heat exchangers).

The effect of using EA in Claus furnace is widely studied in literature (Khudenko et. al, 1993) and the main beneficial aspects are: a) the reduction of process gas flow rate b) longer residence time for the process gas, which favors kinetically-limited reactions; c) less energy and fuel required to preheat the process gas.

The higher combustion temperature in the Claus furnace speeds up kinetically-limited reactions, which means that unwanted elements in Claus feed such as ammonia (NH₃) and BTX (benzene, toluene, and xylene) aromatics are broken down more efficiently. It boosts endothermic reactions in the Claus furnace, such as thermal H₂S splitting, which increases H₂ content in the process gas.

At present, most oxygen is produced from air by cryogenic separation and pressure swing adsorption.  Here a new method is proposed, which is very simple and requires few equipment. The economical evaluation of the application of the proposed process for producing EA, to Claus process, has demonstrated that it is feasible but not convenient. Matlab and Aspen Hysys were used for simulations and system sizing.

* 1. EA production

The most mature technologies for oxygen production are cryogenic distillation and pressure swing adsorption (PSA) (Belaissaoui et al., 2014). The first one enables to produce high purity O2 (>99%) at a large scale (beyond 100-300 tons/day) while pressure swing adsorption (PSA) produces O2 concentration around 95% and is suitable for small to medium scale plant (20-100 tons/day). These techniques are however still considered as too energy intensive. Membrane separation technique has shown growing interest during the last decades as an alternative approach (Bernardo et al. 2009, Bernardo et al., 2013). Oxygen separation membranes have been indeed reported to be potentially attractive and competitive for medium O2 purity (25–40%) and small scale plant (10–25 tons/day).

The proposed method is based on adsorption and desorption of oxygen in water, taking advantages of the higher oxygen solubility in water compared to nitrogen (Manenti and Pirola, 2014). This new method is completely different from the traditional methods found in literature for the production of oxygen and nitrogen. Traditional methods are, in fact, designed, developed and optimized to obtain pure oxygen and byproducts consisting of pure nitrogen, and in some cases, also pure argon (air distillation). The system behaves similar to a “Pressure swing absorption” in which the absorbent element is not a fixed bed of solid material but it is substituted by water. The experimental set up used to study and optimize the process has been described by Galli et al., 2017. This method basically exploits the ability of water to absorb and desorb more oxygen in respect to nitrogen at different temperature and pressure. The solubility of these gases in water is very low and Henry’s law can be used for better simulate the system.

If the pressure of the system is increased, the solubility of gases is also increased. Temperature has, of course, a detrimental effect. In order to maximize the content of gases that are absorbed, the best condition of the system are high pressure and low temperature. Desorption, on the contrary, is maximized by adopting low pressures and high temperatures. In the best case, the EA produced with this method can have a concentration of O2 around 33-34%. Lastly this method does not produce byproducts because the air exiting from the absorption stage, due to the low solubilities of nitrogen and oxygen in water, is substantially equal to atmospheric air and so it can be recycled in order to reduce the power needed to compress atmospheric air before absorption stage.

* 1. Numerical Methods

It has been developed an ideal a simulation of the proposed plant (with Aspen Hysys) in order to evaluate the fixed costs and the operating costs of the plant to be compared to that of the same plant using traditional EA production methods.

The flow-diagram of the plant is reported in Figure 1:



P 100

K 100

TEE 101

Water

Air

E 101

E 100

E104

E102

V 100

T 100

Figure 1: EA production plant

Water and air meet each other in an adsorber (T100) . Enriched water is then sent to a flash (V 100) for removing adsorbed oxygen from water obtaining enriched air. Spent air and water are recycled back to the process.

The absorber equipment was considered with 10 theoretical trays in order to be sure that thermodynamic equilibrium was reached. The splitter TEE-101 is used to purge air. For air recycle it was selected a purge equal to 10% of the flowing air. This is necessary: 1) to avoid the accumulation of water vapor in the stream of air, restoring the oxygen in concentration as high as possible in order to minimize the volume of the absorber; 2) to minimize the volume of water needed (higher oxygen concentration higher driving force for absorption); 3) to avoid air flow increasing to be compressed. Heat exchanger E-100 and E-101 are used to cool streams of air and water to 20°C, while E-102 is used to heat the water stream to the design temperature using low pressure steam. K-100 is the compressor and P-100 is the pump, both of these have an efficiency of 75%. For the simulation it was considered water and air supplied at the plant at 20°C and 1 atm.

The operating and the capital costs (OPEX and CAPEX), were calculated according to the Guthrie method (Guthrie, 1969; Guthrie, 1974). Eq. (1) was used for the calculation of CAPEX:

Cost of equipment =  (1)

where:

=purchased cost for base condition



FP= correction factor that depends on the operating pressure

FM= correction factor that depends on the construction material (=1 for carbon steel)

K1, K2, K3= constant that are functions of the equipment considered

A = characteristic property of the equipment considered

FP can be determined by equation 2:

 (2)

where:

C1, C2, C3= constant that are functions of the equipment considered

P = relative pressure of the system

Values of K1, K2, K3, C1, C2, and C3 are reported in table 1:

Table 1: constant for CAPEX calculation

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Equipment | K1 | K2 | K3 | C1 | C2 | C3 |
| Compressor | 2.2897 | 1.3604 | -0.1027 | 0 | 0 | 0 |
| Heat exch. (p>5 barg) | 4.3247 | -0.303 | 0.1634 | 0.03881 | -0.11272 | 0.08183 |
| packing | 2.4493 | 0.9744 | 0.0045 | 0 | 0 | 0 |
| Horizontal vessel | 3.5565 | 0.3776 | 0.0905 | 0 | 0 | 0 |
| Vertical vessel | 3.4974 | 0.4485 | 0.1074 | 0 | 0 | 0 |
| Pump (P > 10 barg) | 3.3892 | 0.0536 | 0.1538 | -0.3935 | 0.3957 | -0.00226 |

The costs of equipment have been actualized through equation 3:

Cost of the equipment = [$] (3)

where CEPCI of 2001 is 397 (CEPCI CURRENT YEAR is referred to 2017 and is 540). In order to estimate the operating cost the utilities consumption have to be multiplied by the annual hour of working for the plant and by the utilities cost:

Annual utility cost = nworking hours CostutilityQ (4)

Where:

nworking hours = 8000 hours at year

Costutility= utility cost

Q = utility consumption in 1 hour

Values of utilities cost used in the evaluation are reported in Table 2:

Table 2: equipment cost

|  |  |
| --- | --- |
| Equipment | cost |
| Air supply | 0.0035 | $/m3 |
| Low pressure steam | 0.02929 | $/kg |
| Water | 0.000067 | $/kg |
| Electricity | 0.156 | €/kWh |

To evaluate the economic convenience of the new method it was considered a market price of pure oxygen of 6 €/stdm3 for oxygen, the price for EA of the same composition obtained from the simulation can be calculated by simple weighted summation (0.57 €/stdm3 for EA with 28% oxygen). The cost of production of EA with the proposed method can be easily determined by dividing the total annual cost (fixed cost divided for the number of life years of the plant plus annual operating cost) by the total amount of stdm3 of EA produced in 1 year. For the calculus, it was considered a lifetime of the plant of 20 year and 8000 hour/year operating plant.

* 1. Case Study: Claus Process

It was decided to study the feasibility and the economic aspect of producing EA with the new proposed method applied to a Claus plant of small size (about 10 tons of H2S treated each day). Claus process is characterised by the following reactions:

3 H2S + 3/2 O₂ → 2 H2S + SO₂+ H2O (5)

2 H2S + SO₂ → 3 S + 2 H2O (6)

The global mechanism of the process is, therefore:

3 H2S + 3/2 O₂ → 3 S + 3 H2O (7)

Considering oxygen concentration in air, the air needed to treat 10 ton/day of H2S is 29.2 kmol/h. If EA with 28% oxygen is used the flow rate reduces to 21.9 kmol/h.

* 1. Results and discussion

Two different EA production plants were analyzed: the first-one operates under pressure and with a temperature difference between absorber and flash in order to increase the desorption process. The second-one is a quasi-isothermal process that works at a constant temperature of 20°C and the absorption and desorption process depend only on the pressure differences inside the plant.

* + 1. *Non isothermal process*

The operating conditions which have been considered are: P\_absorber = 10-30-50-75-100 atm; T\_absorber = 20°C; P\_flash = 1 atm; T\_flash = 40-60-80°C; Air/water ratio = 0.35-1 (interval of 0.05, mol/mol). By looking at the sizing results, for the case of 10 atm, the area of heat exchangers and the power needed for the compression are out of scale and so these cases are discarded without making the economic analysis.

Figure 2: CAPEX and OPEX for EA production versus air/water ratio varying absorption pressure (T flash 40°C)

For the other cases the results of economic analysis are reported in Figure 2, where only the data at 40°C are reported because the lines at the other simulated temperature were practically coincident. The costs related to compressor were calculated in a different way respect to other equipment. In fact, the limit reported for determining the cost for compressor is 3000kW and often this value is exceeded. When this happens, 2 equal compressor having half of the original power were considered.

From the results, it can be observed that the proposed method is effectively cost convenient comparing to the use of enriched air obtained from air mixing with pure oxygen (0.29 €/stdm3 versus 0.57 €/stdm3). All the analysed cases produce lower costs than the traditional method and so the proposed plant is feasible and economically advantageous. The equipment sizing and the relative costs are reported in Table 3 for the most convenient configuration that is at 40°C (flash temperature) and 100 atm, 0.35 air/water molar ratio (corresponding to 21.9 kmol/h EA and 62.6 kmol/h water).

Table 3: EA production fixed cost at 40°C flash temperature and 100 atm absorption, 0.35 air/water molar ratio

|  |  |  |  |
| --- | --- | --- | --- |
| Equipment | size | Power kW | Fixed cost (€) |
| Absorber | 6.2 m3 |  | 15803 |
| Flash | 7.4 m3 |  | 9803 |
| E100 | 107 m2 |  | 38146 |
| E101 | 83 m2 |  | 37414 |
| E102 | 12 m2 |  | 23460 |
| E104 | 58 m2 |  | 30091 |
| pump |  | 185 | 52821 |
| compressor |  | 935 | 313664 |
| Total cost (€) |  |  | 521205 |

* + 1. Quasi isothermal plant

The simulation parameters are the following: P\_absorber = 10-30-50-75-100 atm; T\_absorber = 20°C; P\_flash = 1 atm; T\_flash = 20°C; Air/water ratio = 0.3-1 interval of 0.05. The stream exiting from HE-100 can be split and partly used to completely heat the process stream 3 and so the utilities related to HE-101 can be neglected. The results for 30, 50, 75 and 100 atm at a fixed temperature of 20°C are reported in Figure 3:

Figure 3: OPEX and CAPEx for EA production versus air/water ratio varying absorption pressure (T flash 20°C)

Also in this case the proposed process is economically convenient with respect to the traditional method (0.27 €/stdm3 versus 0.57 €/stdm3). In all the cases EA production cost decreases by pressure increase. This occurs because, by increasing pressure more oxygen is dissolved in water and so less water is required to reach desired production of EA. The production cost of EA increases with the air/water ratio because it increases the amount of air that has to be compressed and so the relative cost for compressor and compression. The equipment sizing and the relative costs are reported in Table 4 for the most convenient configuration that is at 100 atm, 0.4 air/water molar ratio (21.9 kmol/h EA, 54.8 kmol/h water).

Table 4: EA production fixed cost at 20°C flash temperature and 100 atm absorption, 0.4 air/water ratio

|  |  |  |  |
| --- | --- | --- | --- |
| Equipment | size | Power kW | Fixed cost (€) |
| Absorber | 6.2 m3 |  | 21615 |
| Flash | 7.1 m3 |  | 13068 |
| E 100 | 118 m2 |  | 39529 |
| E101 | 0.37 m2 |  | 26580 |
| pump |  | 176 | 45047 |
| compressor |  | 1019 | 338839 |
| Total cost (€) |  |  | 484680 |

* 1. Conclusions

Here a new process for EA production is proposed. It is based on a very simple concept and equipment. A possible application to Clauss process has been studied. The two analyzed process configurations show comparable CAPEX and OPEX costs, with a slightly better performance for the isothermal case (0.27 €/stdm3 versus 0.29 €/stdm3). In both the cases, the economic assessment of the application of the new proposed process for EA production to the case of a small size Claus plant showed its feasibility and economic convenience. These results depend obviously on the assumptions that have been performed relative to oxygen price and equipment costs. Changing market could produce different scenarios. Finally an economical comparison should be also made with PSA systems. It has also to be observed that transportation costs of pure oxygen have not been taken into account in calculating the cost of enriched air to be compared with that obtained from the new process.

References

Baukal, C. E., 2013. Oxygen-Enhanced Combustion, CRC Press

Bernardo P., Clarizia G., 2013. 30 Years of Membrane Technology for Gas Separation, Chemical Engineering Transactions, 32, 1999-2004

Bernardo, P., Drioli, E., Golemme, G., 2009. Membrane gas separation: a review/state of the art. Ind. Eng. Chem. Res., 48, 4638-4663

Belaissaoui, B., Le Mollec, Y., Hagi, H., Favre, E.. 2014. Energy Efficiency of oxygen enriched air production technologies: cryogeny vs membranes. Separation and Purification Technology 125, 142-150.

[Galli F](https://www.ncbi.nlm.nih.gov/pubmed/?term=Galli%20F%5BAuthor%5D&cauthor=true&cauthor_uid=29649734)., [Previtali D](https://www.ncbi.nlm.nih.gov/pubmed/?term=Previtali%20D%5BAuthor%5D&cauthor=true&cauthor_uid=29649734)., [Bozzano G](https://www.ncbi.nlm.nih.gov/pubmed/?term=Bozzano%20G%5BAuthor%5D&cauthor=true&cauthor_uid=29649734)., [Bianchi C](https://www.ncbi.nlm.nih.gov/pubmed/?term=Bianchi%20CL%5BAuthor%5D&cauthor=true&cauthor_uid=29649734)., [Manenti F](https://www.ncbi.nlm.nih.gov/pubmed/?term=Manenti%20F%5BAuthor%5D&cauthor=true&cauthor_uid=29649734)., [Pirola C](https://www.ncbi.nlm.nih.gov/pubmed/?term=Pirola%20C%5BAuthor%5D&cauthor=true&cauthor_uid=29649734)., 2017. Production of oxygen-enriched air via desorption from water: Experimental data, simulations and economic assessment. Comp. & Chem. Eng., 102, 11-16.

Guthrie, K, M., 1969, Capital Cost Estimating, Chem. Eng., 76, 114

Guthrie, K, M., 1974, Process Plant Estimating, Evaluation and Control. Solama Beach, CA

Khudenko B.M., Gitman G.M., Wechsler T.E., 1993. Oxygen Based Claus Process For Recovery of Sulfur from H2S Gases J. Environ. Eng., 119(6), 1233-1251

Hendershot, R. ]., Lebrecht, T. D., and Easterbrook, N. C., 2010. Use oxygen to improve combustion and oxidation, Chemical Engineering Progress, 106(7), 57—61.

Manenti, F., Pirola, C., 2014. Process for the enrichment of air, W02014/161713 A1

Richard Turton, R. C., 2012. Analysis, Synthesis, and Design of Chemical Processes, Fourth Edition. Prentice Hall.