Imperial College London



Professor Efstratios PistikopoulosCentre for Process Systems Engineering

Prof. Dr.-Ing. Wolfgang Marquardt Institute for Process Systems Engineering

Capital Cost Evaluation for Optimum Process Design of Cryogenic Air Separation

Diploma Thesis by Robert Pack

London, SS 2012

Contents

1	Intr	duction	
2	Air 2.1 2.2 2.3	eparation Technology Cryogenic Air Separation	4
3	Proc 3.1 3.2 3.3	Process Model Uncertainty in Process Modeling Economic Considerations 3.3.1 Project cost 3.3.2 Profitability measures	
4	4.1 4.2	genic Air Separation Process Model 4.1.1 Distillation Columns 4.1.2 Heat Exchanger 4.1.3 Compressors 4.1.4 Turbine Process Economics	10 10 10
5	Con	lusion and Further Research	11
Bi	bliog	phy	13

List of Figures

2.1	Comparison of Air Separation Technologies [3]	2
2.2	Air Separation Unit	3
2.3	Schematic representation of the PSA process	4
2.4	Gas permeation process	5
3.1	Accumulated cash flows over project life cycle	9

List of Tables

Nomenclature

C_1	Reference equipment cost at time 1	[\$]
C_2	Reference equipment cost at time 2	[\$]
C_B	Reference equipment cost	[\$]
C_E	Equipment cost	[\$]
$index_1$	index at time 1	[-]
index ₂	index at time 2	[-]
М	Equipment specific factor	[-]
Q	Equipment specific quantity	[-]
Q_B	Equipment specific reference quantity	[—]

1 Introduction

Air separation technology, or – more generally speaking – gas separation technology, lies at the heart of the modern process industry. Highly pure oxygen and nitrogen ore uses in many industrial applications. Modern power generation processes, such as the currently developed OXICOAL process, rely on incineration with pure oxygen to produce flue gases with very high carbon dioxide content for further storage. Nitrogen is essential to many widely used processes such as the production of ammonia in the Haber-Bosch synthesis, as fertilizer or in many organic reactions.

2 Air Separation Technology

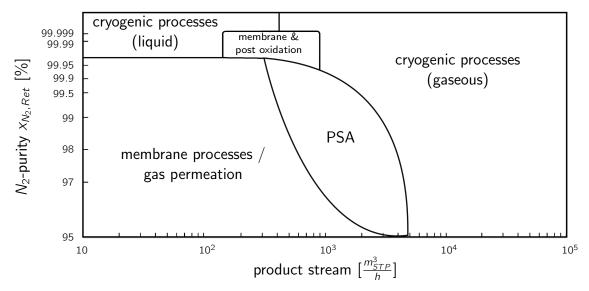


Figure 2.1: Comparison of Air Separation Technologies [3].

There are several ways besides cryogenic air separation that can be employed to separate gas mixtures. In this chapter different competing technologies and their main applications will be discussed. The predominately used technologies are cryogenic distillation, pressure swing adsorption (PSA) as well as gas permeation (GP). In the distillation process the gas is first liquefied. Separation is the achieved by the different concentration differences in vapor and liquid phase. PSA relies on the different affinities of gaseous species to adsorb to certain materials in order to extract a component form a mixture. During gas permeation membranes are used. Each species migrates in different quantities through a given membrane depending on process parameters and membrane structure.

Fig. 2.1 illustrates the most economically viable processes depending on product purity and product stream volume. It can be seen that alternative air separation processes cannot supply the high quality or quantity of the cryogenic process. Due to that cryogenic air separation is thought to be the main supplier of highly pure gases in industrial quantities for years to come [1]. The alternative processes however offer some very appealing characteristics, which make them the favorable choice when lower quantities of product or more moderate purity is required. The cryogenic process is always connected with an considerable energy consumption for the liquefaction and compression. Due to that smaller implementations of the process a very unlikely to yield economically sound solutions to a separation problem.

add citation

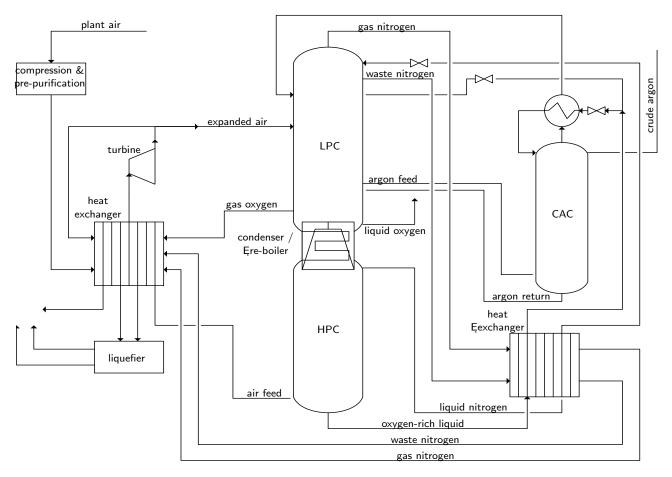


Figure 2.2: Schematic representation of the cryogenic air separation process.

2.1 Cryogenic Air Separation

Cryogenic Air Separation finds applications over a great variety of industries among others refining, petrochemicals, medical, food & beverages and environmental [4]. Furthermore prospective processes for power generation from fossil sources in form of the integrated gaseous combined cycle (IGCC) integrates the air separation process in order to enable more environmentally friendly power generation [2].

As can be seen in Fig. 2.2 double effect heat integrated distillation column lies at the heart of the air liquefaction processes. It consists of a high pressure column (HPC) operating at $0.68\ MPa$ and temperatures below $130\ K$ as well as a low pressure column (LPC) which operates at around $0.13\ MPa$ an comparable temperatures. In order to also attain highly pure argon as a product the process may also include a crude argon column (CAC) which works at slightly lower pressures than the LPC.

The plant air entering the process is initially purified, where carbon and nitrogen oxides as well as solid contaminants are removed, and then compressed to process conditions. The compressed air is then cooled against product streams namely liquefied nitrogen, oxygen and argon. The air stream is then divided into several sub-streams. One of those is fed into the HPC bottom, while another is expanded by means of a turbine and further cooled down through the Joule- Thompson effect. Aside from further cooling energy from the initial compression is thus partially recovered. This expanded air stream is then fed into the LPC. At the bottom of the LPC liquid as well as gaseous oxygen are

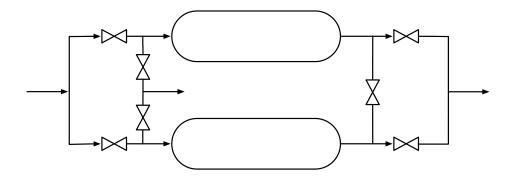


Figure 2.3: Schematic representation of the PSA process.

recovered as desired products. The bottom and top streams from the HPC are made up of an oxygen rich liquid as well as liquid nitrogen. The liquid nitrogen stream is led though an heat exchanger an the fed as reflux into the top of the LPC. The bottom stream is, after heat integration, partially fed into the LPC as well as CAC. From the lower part of the LPC a side stream is drawn and led into the bottom of the CAC. At the same point the reflux from the CAC is fed back into the LPC [5].

2.2 Pressure Swing Adsorbtion

Pressure Swing Adsorption has been employed to separate gaseous mixtures for some time. During the 80's and 90's commercial applications for the production of oxygen or nitrogen have gained more and more attention. Especially the ability to construct very compact units the size of a briefcase, have led to the implementation of PSA processes for treatment of asthma patients or other medical appliances. But also larger scale plants have successfully been utilized, for example in the paper industry during the de-lignation of pulp. It remains true however, that for large scale industrial settings with high product quality demands, cryogenic separation remains the most viable alternative.

Separation is achieved during the PSA process by adsorption of one component in the mixture to a given bed. Once the bed is saturated with a the adsorbing species, it has to be regenerated in order to continue production. The ability to adsorb a certain species is dependent on the system pressure. At higher pressures more gas can be adsorbed then at lower pressures. Thus by reducing the pressure in the reaction vessel, the Adsorbent can be regenerated.

In order to avoid non-continuous processes, two or more reaction vessels are employed. Therefore the saturated vessel can be regenerated, while the other one continues production. By alternating adsorption and regenerating in the different vessels continuous production can be achieved. A schematic for a simple two bed cycle is shown in Fig. 2.3. Ambient air is first led through the first reaction vessel at the elevated pressure. Within the vessel nitrogen is adsorbed until saturation is reached. At that point the ambient air is led through the second vessel. A fraction of the product stream is fed into the first vessel and used as sweep for the regeneration of the adsorbent at lower pressure.

Depending on the size of the process two different pressure level are used. One cycle adsorbs the nitrogen at a pressure of approximately 7.5 bar while regeneration is done at ambient pressure. Within

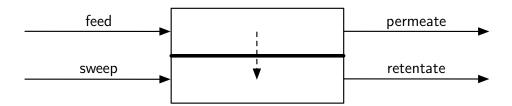


Figure 2.4: Gas permeation process.

the alternative approach adsorption occurs under ambient condition, while for the regeneration step a vacuum pump reduces the vessel pressure. This process is the called Vacuum Pressure Swing Adsorption (VPSA).

An important role when designing the product is the choice of the adsorbent. For almost all current applications of PSA alumosilicates or zeolithes have been designed, tailored to the specific separation task. Their main advantages include a high selectivity towards a specic gas to be adsorbed as well as a very homogenous distribution of diameters in the molecular sieve.

2.3 Gas Permeation

find paper: DOI: 10.1002/cite.330480804

add reference: ISBN-10: 354034327X

The separation of mixed gases by membrane process is called gas permeation. Its main strength in comparison with alternative processes are the low energy consumption and the possibility to produce flexible mobile units. As mentioned before it is not however capable of producing high quantity highly pure product streams. As Fig. 2.1 illustrates the main application for the gas permeation process are small to moderate product streams at intermediate purities.

Fig. 2.4 shows the schematic for a single stage membrane unit. Within the feed stream the gaseous mixture is fed into the unit, which can quickly be implemented. Within the unit one or more species migrate favorably through the membrane. In this case mostly dense polymer membranes are employed used. There have been some impressive results with metallic membranes, but due to the very high material costs they have not been adapted by the industry. Furthermore, since gaseous phases often have rather small molecular species, porous membranes cannot achieve desired separation. The driving force the separation process is a difference in partial pressure or species activity across the membrane. According to the molecular structure of each species, the structure of the separating membrane as well as the process parameters pressure and temperature, they permeate through the membrane in different quantities.

The process of permeation can be subdivided into three separate steps. Sorption at the membrane / feed interface, diffusion through the mostly dense polymer membrane and finally desorption at the permeate side of the membrane.

3 Process Design

Once a particular reaction or production sequence has been developed in a laboratory it needs to be scaled up to produce the desired product in quantities large enough to meet market demand to a price that allows competative prices. This is where process design comes into play. At the begin of the design process often only the raw material as well as the desired products, along with the necessary chemical reactions are specified. It is then the task of the process engineer to find a series of production steps which lead to the production of this product. Each step denotes a specific function and the connected functions form a process. At the end each specific function has to be assigned a specific technical realization.

Usually there are numerous options available to perform certain tasks and in order to be realized any endeavor will need to yield acceptable profits. Different options will therefore have to be compared from an engineering and an economic standpoint alike. For complex processes the amount of possible options becomes enormous. Too many to be manually examined and evaluated.

Number of options for separation problem – ref douglas

Process Engineers have to rely on heuristics to limit the number of options and identify the most promising candidates for further studies. These candidates can then be compared in terms of economic performance. In order to do so one has to rely on simulation studies and experiments. As experiments and the construction of pilot plants are very costly the aim is to minimize those. With the rise in available computing power the numerical simulation of processes has become a very powerful tool to support the design process and has the ability to replace numerous experiments. Not only can possible options be evaluated but also can optimal process configurations from a limited pool of options be generated.

To conduct simulation studies first a process model needs to be created. This models in its most general case is a set of partial differential and algebraic equations. When formulating the model great care needs to be applied, as any simulation study can only be as accurate as the underlying model. The process engineer is faces with the task to find an adequate representation of the physical system which delivers meaningful results within an reasonable amount of time. Further enhanced is this problem when the model is to be used in model predictive control, where (approximate) solutions of complex systems might need to be available within seconds or fractions of a second.

In the following sections some general considerations on the physical and economic modeling of chemical process will be given, before in the next chapter those will be applied to real-life problem at hand. AS uncertainty

3.1 Process Model

3.2 Uncertainty in Process Modeling

3.3 Economic Considerations

Aside from question wether a certain process is capable of producing products according to its specifications, it needs to be investigated if it does so in an economically viable manner. The modeling of process economics is a powerful tool to estimate project profitability. The evaluation of process economics has three major aims in the design phase.

- · Compare design options with regard to profitability.
- · Economically optimize a given design.
- · Estimate project profitability

In any case the total cost of the project as well as the cash flow structure will have to be analyzed to supply an accurate estimate of the economic conditions. Furthermore an adequate measure to compare and analyze a project in economic terms needs to be employed.

The following sections will first describe how to estimate the total project cost in different stages of the design process. Subsequently different ways of measuring a projects profitability will be discussed.

3.3.1 Project cost

An important factor in every given project is the total cost. During the design of a chemical process many important aspects of the future cost structure are unknown, as the final design is in development. In general the total cost of implementing and operating a production site can be broken down into several subcategories.

- Battery limit investment
- Utility investment
- Off-Site investment
- · Engineering fees
- · Working capital

We will now look closer at each of these subcategories.

Battery limit investment

denotes all investments necessary to have all required equipment for process operations installed on-site. This includes structures necessary to house the process as well as delivery and installation of all individual assets. One major part of these cost will the the process equipment. As the exact manufacturers and models of the equipment will not be known in early design stages, a different approach has to be chosen. Various process parameters such as temperatures, pressures and handled volumes will have an effect of the required equipment. High pressure tanks will most likely be more expensive as stronger materials and thicker walls will be necessary. Each piece of equipment will have an specific feature that most influences its cost. For vessels and reactors this might be volume, while for heat exchangers the required heat exchange area. The equipment price C_E can be approximated by a simple power law

$$C_E = C_B \left(\frac{Q}{Q_B}\right)^M. ag{3.1}$$

A reference price C_B is multiplied by the determining quantity Q normalized to a reference state Q_B and raised to the power M specific to each piece of equipment. Reference prices for various installations can be obtained from literature.

add reference

As the overall price structure may change dramatically over time these prices will have to be adjusted to current time. To do so several indices have been developed

$$\frac{C_1}{C_2} = \frac{index_1}{index_2}. (3.2)$$

While for each index an arbitrary reference year is chosen. Among the most common indices are the Marshall & Swift index (1926: index = 100) or the Nellson-Farrar-Index (1946: index = 100)

As mentioned before aside from the mere size of the equipment the process conditions will also affect the price. The predominant factors to that respect are pressure, temperature and the question wether corrosive or reactive media will be present.

3.3.2 Profitability measures

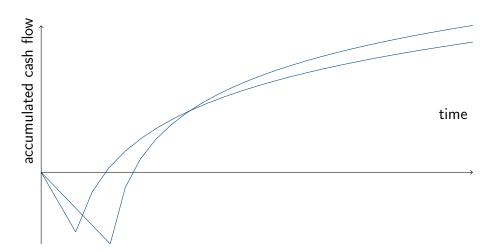


Figure 3.1: Accumulated cash flows over project life cycle.

4 Cryogenic Air Separation

- 4.1 Process Model
- 4.1.1 Distillation Columns
- 4.1.2 Heat Exchanger
- 4.1.3 Compressors
- **4.1.4 Turbine**
- 4.2 Process Economics

5 Conclusion and Further Research

Todo list

add citation	2
find paper: DOI: 10.1002/cite.330480804	5
add reference: ISBN-10: 354034327X	5
Number of options for separation problem – ref douglas	6
add reference	8

Bibliography

- [1] W. F. Castle. Air separation and liquefaction: recent developments and prospects for the beginning of the new millennium. *International Journal of Refrigeration*, 25(1):158–172, 2002.
- [2] P. Mahapatra and B. W. Bequette. Process design and control studies of an elevated-pressure air separations unit for IGCC power plants: American Control Conference (ACC), 2010: American Control Conference (ACC), 2010 DOI -. American Control Conference (ACC), 2010, pages 2003–2008, 2010.
- [3] R. Prasad, F. Notaro, and D.R Thompson. Evolution of membranes in commercial air separation. *Journal of Membrane Science*, 94(1):225–248, 1994.
- [4] Avinash R. Sirdeshpande, Marianthi G. Ierapetritou, Mark J. Andrecovich, and Joseph P. Naumovitz. Process synthesis optimization and flexibility evaluation of air separation cycles. *AIChE Journal*, 51(4):1190–1200, 2005.
- [5] Yu Zhu, Sean Legg, and Carl D. Laird. Optimal design of cryogenic air separation columns under uncertainty: Selected papers from the 7th International Conference on the Foundations of Computer-Aided Process Design (FOCAPD, 2009, Breckenridge, Colorado, USA. *Computers & Chemical Engineering*, 34(9):1377–1384, 2010.