

EXERGY ANALYSIS OF CRYOGENIC AIR SEPARATION

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ABSTRACT. An exergy analysis is performed to analyse the possibilities of fuel saving in the cryogenic distillation process, which is the main method of air separation. It is shown that more than half of the exergy loss takes place in the liquefaction unit and almost one third in the air compression unit. Minor exergy losses are taking place in the distillation unit and the main heat exchanger. The major cause of exergy loss is the use of compressors and to a lesser extent the use of turbines. Especially, the relative low rational efficiency of the turbines operating in the cryogenic region is striking. Improvements are suggested which save one fourth of the exergy loss. For more substantial reductions of the exergy losses in air separation alternative processes have to be used or developed.

INTRODUCTION

In an energy analysis, based on the first law of thermodynamics, all forms of energy are considered to be equivalent. This has the disadvantage that the quality loss of energy is not taken into account. For example, the change of the quality of thermal energy as it is transferred from a higher to a lower temperature is not displayed in an energy analysis. It shows the energy flow to be continuous. An exergy analysis, based on the first and second law of thermodynamics, shows the thermodynamic perfection of a process, including all quality losses of materials and energy, including the one just described. The definition of exergy is the maximum obtainable potential of work of a stream or substance in relation to the environment.

AIR SEPARATION

The separation of air into its internal components is carried out for industrial and medical use. The greatest use of nitrogen is as an inert blanking gas and as a reactant in chemical processes. Oxygen is used both for industrial and medical purposes. There are three methods of air separation commercially available: the cryogenic distillation process, the pressure swing adsorption (PSA) process and the membrane separation process. The cryogenic distillation is used when high purity of the products is needed. The PSA process becomes interesting from a commercial point of view when a nitrogen flow between 10 and 100 m³/hr is needed with a purity of 98 to 99.5 vol. %. Membrane separation is used for small flows, less than 10 m³/hr, and low purity, lower than 98.5 vol. % [1]. Cryogenic distillation is required, when the products are needed in a liquid form. In this article the most widely used air separation process, the cryogenic process, has been analysed.

CRYOGENIC PROCESS

Method

To analyse the cryogenic process a simulation of a real plant has been made. The simulation has been performed by the flow sheeting program Aspen Plus. For the calculation of exergy in Aspen Plus a special module has been used, named ExerCom, which has been developed by Stork Comprimo [2] in co-operation with Delft Technical University.

Plant

The analysed plant uses the principle of two columns separation. This is based on a low and a high pressure distillation column. The condenser of the high pressure lower column is cooled by the reboiler of the low pressure upper column. This principle is widely used for cryogenic air separation plants. The flowsheet of the plant is shown in Figure 1. The incoming air is compressed to 6.2 bar and after cooling in the spray cooler (SC) water and coal dioxide are removed by adsorption in the molecular filters. Subsequently, the air is cooled in the main heat exchanger (MHE) to $-172\text{ }^{\circ}\text{C}$ and enters the lower column (LC), which has 54 stages. Here, the air is separated into the top product nitrogen, which is partly liquefied in the condenser and the bottom product, which is a mixture of 38 vol.% oxygen, 60 vol. % nitrogen and 1.6 vol. % argon. The gaseous part of the nitrogen is liquefied in a special section. Here, the nitrogen is compressed to 46 bar. The 46 bar compressor is driven by the hot expansion turbine (HET) and the 36 bar compressor by the cold expansion turbine (CET). The liquefaction of the stream takes place in heat exchanger 2 (H.E. 2). Further cooling of the liquid nitrogen takes place in the throttling valve (TV). The nitrogen is almost completely liquefied after passing this unit and enters the lower column again. The bottom product and the liquid nitrogen leaving the lower column are throttled to ca. 1.5 bar and enter the upper column (UC), which has 96 stages. Of this column the top product is gaseous and liquid nitrogen and the bottom product is gaseous and liquid oxygen. One of the side products is unpurified argon, consisting of argon with oxygen and nitrogen. Most of this oxygen and nitrogen returns from the raw argon distillation column to the upper column. The other side product is purge gas, which is used to clean the molecular filters. It consists mainly of nitrogen and the gas is heated to $170\text{ }^{\circ}\text{C}$ before cleaning the filters. The top product of the raw argon distillation column (RA) enters the argon purifying unit, where it is compressed to 3 bar and deoxygenated by burning the oxygen with hydrogen. After cooling, separating the water and further cooling to $-180\text{ }^{\circ}\text{C}$ the argon is further purified in the pure argon distillation column (P.A.). Compression of the products to the desired pressure is left out in this analysis. The flow and product specification are displayed in Table 1. Because of the flexibility of the plant variations of the flow are possible. The analysis has been performed with the given flow in Table 1.

Table 1. Flow and product specification

Components	flow (in kg/s)	purity (in vol. %)
Air	16.39	--
Gaseous Oxygen (GOX)	2.82	99.5
Liquid Oxygen (LOX)	0.70	99.6
Gaseous Nitrogen (GAN)	6.18	99.95
Liquid Nitrogen (LIN)	2.86	99.999
Liquid Argon (LAR)	0.13	99

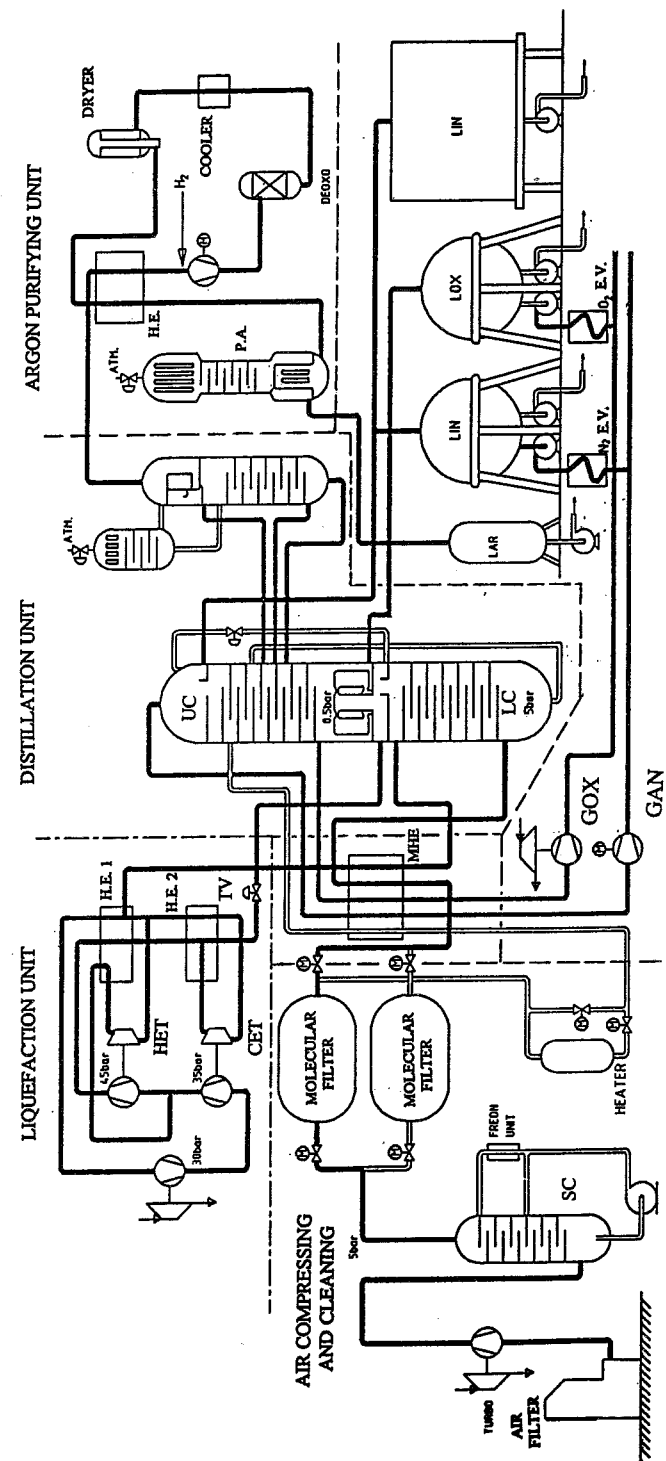


Figure 1 Flowsheet of the analysed cryogenic air separation plant

All pressures listed in the flowsheet are relative pressures

EXERGY ANALYSIS

The fundamentals and method of exergy analysis are presented in the books of Kotas [3] and Szargut et al. [4]. The rational efficiency is used to show the degree of thermodynamic perfection of the processes and is defined as a ratio of the desired exergy output to the exergy used.

$$\psi = \frac{\dot{E}_{\text{desired output}}}{\dot{E}_{\text{used}}} = \frac{\dot{E}_{\text{desired output}}}{\dot{E}_{\text{desired output}} + \dot{I}}$$

The exergy used equals the desired exergy output and the exergy loss. The concept and use of the rational efficiency are explained in Kotas [3] and Cornelissen et al. [5].

Air compressor and cleaning unit

The main exergy loss, 1677 kW, is caused by the compression of the air to 6.2 bar. The exergy loss of the steam turbine, which delivers the required 4.3 MW of power for the compressor, is 708 kW. The consumption of steam of 400°C and 40 bar is 15.5 ton a hour. The rational efficiency of the steam turbine is 0.86. For cooling the air to 7°C the electricity use is 110 kW. Most of the exergy increase due to the cooling of the air is lost in the molecular filter, because the air is here almost heated to environmental temperature. By the heating of the purge gas to 170°C with steam of 210°C and 11 bar and dumping the gas into the environment 225 kW of exergy is lost. The desired output is considered to be the cleaned compressed air, resulting in a rational efficiency of 0.48.

Main heat exchanger (MHE)

The exergy losses are caused by temperature difference between the hot and cold streams and pressure losses. The mean temperature difference is 4.2 K. The rational efficiency of heat exchangers is defined as the exergy increase of the cold streams divided by the exergy decrease of the hot streams.

Distillation unit

An exergy loss of 82 kW is caused by the temperature difference of 1.1 K between the reboiler of the upper column and the condenser of the lower column. The throttling process between the lower and upper column causes an exergy loss of 125 kW. An exergy loss of 32 kW takes place in the heat exchanger (not displayed in figure 1), which cools the products of the lower column before going into the upper column. The rational efficiency of this heat exchanger is 0.88. The exergy loss in the lower column (LC) is 62 kW and the exergy loss in the upper column (UC) and raw argon column is 436 kW. Of the exergy loss in the raw argon column 108 kW is caused in the condenser by the temperature difference of 2.8 K between the coolant and the top of the column. The desired output is considered to be the chemical exergy increase due to the separation. This result in a rational efficiency of 0.53. It can be argued that the definition of this efficiency does not give a complete view, because the transformation of the mechanical component into the thermal component of exergy is not taken into account in the desired output.

Liquefaction unit

The exergy losses and the rational efficiencies of the different components are displayed in Table 2. For the compression of the nitrogen to 30 bar a five stages compressor with intercooling is used. The steam turbine, which delivers the needed 6.0 MW for the compressor, uses 22 ton steam a hour of 420°C and 40 bar. A capacity mismatch between the compressor, which compress to 46 bar, and the hot expansion turbine results in a great exergy loss. Probably, there is a recycle stream along the compressor. The rational efficiency of the turbines

is defined as the work divided by the exergy decrease of the incoming and outgoing flow. The relative low efficiency of the turbines is caused by the fact that the expansion of the flows takes place under the environmental temperature. The temperature difference between the isentropic temperature and the real outlet temperature leads to a great exergy loss due to the low temperature. Especially, in the case of the cold expansion turbine (CET), where the outlet temperature is -177 °C. The throttling process in the valve (TV) causes a temperature decrease of 3.4 K. The low exergy loss in the valve is reached because the flow enters the valve in the liquid phase and leaves the valve almost completely liquefied. Because no distinction is made between the thermal and mechanical component it was not possible to define a desired product and so no efficiency could be calculated. The mixing of flows causes a minor exergy loss. No desired product can be defined in the case of mixing. The desired output of this unit is seen as the exergy increase of the outgoing flow compared to the incoming flow because of the cooling and liquefying of the nitrogen.

Table 2 Exergy losses in the liquefaction unit

Unit	exergy losses (in kW)	rational efficiency
Five stages compressor	1 965	0.67
Steam turbine	1 000	0.86
Compressor to 37 bar	205	0.70
Compressor to 46 bar	141	0.69
Capacity mismatch	344	
Hot expansion turbine	241	0.77
Cold expansion turbine	428	0.61
Heat exchanger 1	256	0.72
Heat exchanger 2	173	0.90
Mixers	5	----
Throttling valve	74	----
Total	4 832	0.25

Argon purifying unit

The exergy loss in the heat exchanger (H.E.) and compressor is 1.2 kW and 2.9 kW, respectively. The deoxygenating of the stream with hydrogen with a exergy of 65 kW causes an irreversibility of 27 kW. The exergy loss taking place due to the cooling of argon flow from 950°C to 15°C leads to an exergy loss of 43 kW. The heat is not used somewhere else. The exergy loss in the pure argon distillation column is 10 kW. A purge stream of 0.8 kW leaves the column at the top. The rational efficiency of this unit is 0.017, when the chemical exergy increase of the argon due to the purifying is seen as the desired product.

Table 3 Results of the exergy analysis

Unit	exergy losses (in kW)	rational efficiency
Air compressor and cleaning	2 810	0.48
Main heat exchanger	333	0.86
Distillation unit	736	0.53
Liquefaction unit	4 832	0.27
Argon purifying unit	85	0.02
Total	8 796	0.29

Total

The overall exergy loss is 8 796 kW as can be seen in Table 3. The total exergy of the products is 3 514 kW, resulting in an overall rational efficiency of 0.29. The efficiency is so high due to the great physical exergy of the products of 2 765 kW, mainly caused by the physical exergy of the liquid products, which is 2 602 kW. If only the chemical exergy of the products is seen as the desired output, the rational efficiency becomes 0.073.

RESULTS

More than half of the exergy loss is taking place in the liquefaction unit, while almost one third is lost in the air compression unit. Minor exergy losses are taking place in the distillation unit and heat exchangers. The greatest exergy losses are caused by the compressors and to a lesser extent by the turbines. The relatively low rational efficiency of the turbines operating in the cryogenic region is striking, while the efficiency of the heat exchangers is very high.

IMPROVEMENTS

By using the excess work in the case of the capacity mismatch 344 kW can be saved. The increase of the polytropic efficiency of the air compressor from 0.70 to 0.85 will decrease the power use by 880 kW. This will give an associated exergy saving in the steam turbine of 139 kW. The increase of the polytropic efficiency of the nitrogen compressor from 0.75 to 0.85 leads to a decrease of the power use by 759 kW. There gives also an associated exergy saving of 108 kW in the steam turbine. The rational efficiencies of the both compressors becomes 0.77. The increase of the polytropic efficiency of 0.83 of the cold expansion turbine to the same value as the hot expansion turbine, will give an exergy saving of 75 kW and results in a rational efficiency of 0.66 for the cold expansion turbine.

The rational efficiency of the heat exchangers is high to very high. So the possibilities for exergy saving are very limited. Only the exergy loss in heat exchanger 1 of the liquefaction unit could be halved by improving the heat integration. This would lead to a exergy saving of about 125 kW.

A further improvement could be obtained by choosing different operating pressures in the lower and upper column. If the lower column operates near atmospheric pressure and the upper column under atmospheric pressure to accomplish the necessary temperature difference between the lower condenser and the upper reboiler the exergy loss due to the compression could be reduced. To compress the products to environmental pressure will require less power than the air compression, because 1/5 of the flow of the outgoing stream is liquid. So around 1/5 of the exergy loss of the air compressor can be saved, leading to a saving of 400 kW. However, the temperature of the columns has to be decreased by around 15 K. This will cause an extra exergy loss. More research has to be done to determine the optimal operating pressure for the columns from the viewpoint of exergy saving. Furthermore, a pressure below environmental pressure can cause difficulties of obtaining the high purity of the products.

CONCLUSIONS

The exergy analysis of the cryogenic air distillation plant has pinpointed and quantified the exergy loss in the different plant sections. The greatest amount of exergy loss is caused by the compressors. This exergy loss can be reduced by almost a half by using better compressors. Including other suggested improvements the exergy loss can be reduced by 25%. However, the cryogenic air separation unit itself is well designed from an exergetic point of view and for a further improvement of the rational efficiency of air separation alternative processes have to be used or developed.

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