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# Analysis of the applicability of adsorption oxygen generators in the field of industry and power engineering

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**Abstract**

Adsorption air separation technologies can be used to generate several hundred tons of oxygen per day. The basis of adsorption technology is the variable absorptive capacity of the adsorbent, which depends on temperature and pressure. The driving force is given by the difference between the actual and the equilibrium concentration of the substance adsorbed on the surface of the adsorbent. There are two main technologies: Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA). PSA methods require electricity to be supplied to the compressor or vacuum pump while the TSA method involves heating the adsorption bed during the regeneration stage. There are also combinations of these processes. In the case of mixed methods, the adsorption process takes place under elevated pressure, whereas regeneration takes place under vacuum or at elevated temperature. The article presents an economic analysis of oxygen production from air by pressure and temperature adsorption methods. We analyzed the possibility of using waste and cogenerated heat from a power station. We specified the effect of the adsorption technology on purity and pressure of the generated oxygen. We analyzed the possibility of using adsorption air separation methods in various fields of industry and energy sector.

*Keywords:* Oxygen, Adsorption, Energy Engineering Introduction

## 1. Introduction

Oxygen for industrial purposes is generated through the process of condensation and distillation of atmospheric air at air separation units (ASU). Membrane-based and adsorption techniques are used to obtain lower purity oxygen.

In cases of oxygen separation for energy purposes (in quantities closely correlated to produced electricity), the energy consumption of the process is a key factor. Furthermore, it is important whether the energy supplied to air separation units may take other forms (for example thermal energy). If thermal energy can be used this opens the way for air separation to be coupled with cogeneration and heat derived from solar collectors. When a power plant is required to work at varied loads (which can be caused by increased shares of renewables in the energy mix), it is also reasonable to examine the possibility of accumulating energy in air separation products, in particular liquefied oxygen, nitrogen, argon and compressed gases.

With respect to oxygenic combustion, the efficiency of an individual installation is the key criterion when selecting the air separation method. Assuming 500 metric tons of oxygen per day to be an economically reasonable threshold for adsorption installations to work efficiently, power units exceeding 25 MWe should be linked with cryogenic air-separation installations. Pilot installations, laboratory installations and oxygenic combustion installations at units with minor powers (distributed cogeneration units, waste incineration plants, steelworks and oth-

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ers) may be supplied with oxygen from membrane-based installations.

Air separation through adsorption is based on a selection of sorbents for which the maximum level of adsorption of individual ingredients is varied. Usually, for the purposes of calculations and selection of sorbent, the assumption is made that the air is a bi-component mixture of nitrogen and oxygen. Other air components are considered to be pollutants in product fluxes. This simplification is adequate for selecting a sorbent in the production of oxygen at concentrations up to 95%. When a higher level of purity is required, other air components need to be factored in.

Nitrogen-selective sorbents are most commonly used, because they can achieve nitrogen adsorption at levels several times higher than oxygen adsorption. If air is passed through them, you can obtain a condensed level of air concentration at non-adsorptive fluxes. However, the process of adsorption is a non-equilibrium process and, thus, the adsorption method of air separation is not a continuous process. It takes place until the beds are saturated with adsorbed substances, followed by a process of regeneration (desorption). In Swing Adsorption (SA) coupled adsorption tanks are used to obtain a relative level of continuity of the process. The process of separation is conducted in only one tank at a time, while the other tank has its beds regenerated.

Currently, regeneration technology is one of the most popular methods of air separation. At relatively low energy costs, it produces oxygen of sufficient purity for oxy-fuel and medical applications. Swing Adsorption solutions deliver oxygen with purity of up to 95% (argon 5%) when nitrogen-binding sorbents are used (for example zeolite sorbents 5A, 13X) and up to 70...75% when oxygen-selective sorbents are used (for example AgBr, AgI powdered sorbents) [1]. There are also works (studies) exploring adsorption technology for oxygen production at purity levels exceeding 97% [2] and even 99% [3]. These are complex processes based on the application of multi-stage VPSA + CMS technologies where a product of varied-pressure oxygen adsorption from the air at highly-efficient nitrogen-selective sorbents (for example LiX, LiAgX lub LiCaX) is fed to extra-cleaning beds made of carbon molecular sieves (CMS, Carbon Molecular Sieves).

### *1.1. Energy needed to produce oxygen*

There are 2 basic categories of methods of adsorption separation of gas mixtures. The first category—based on varied pressures—utilizes the different absorption by adsorption beds at different pressures. The VSA (vacuum swing adsorption) and PSA (pressure swing adsorption) methods fall into this category. In these methods the process of adsorption is conducted under pressure exceeding the pressure for the process of bed regeneration. The only difference is that VSA is conducted between under-pressure and atmospheric pressure and PSA—between atmospheric pressure and over-pressure. The second category—based on varied temperatures—makes use of different absorption by adsorption beds at different temperatures. The TSA (temperature swing adsorption) method falls into this category. In this method the process of adsorption is performed at low temperatures (for example ambient temperature), then the process of bed regeneration is performed at elevated temperatures.

Appropriate conditions of running the process of separation of gas mixtures are selected, among others, on the grounds of adsorption isotherms.

The essential difference between the VSA, PSA and TSA methods, apart from the type of energy consumed for the process, refers to the time duration of an individual adsorption circle. An adsorption circle in varied-temperature technology generally takes several times longer than in varied-pressure technology [4]. This is due to the high level of thermal inertia of adsorption beds (which are mostly mineral or ceramic). As in the TSA method the most time-consuming parts are regenerating the sorbent and preparing it for the start of the next process stage, an increased number of adsorption columns within one set would be required to achieve greater efficiency in oxygen production. In the PSA method it is difficult to obtain a high level of product purity when there is a low concentration of the required substance at feeding fluxes. Varied-temperature adsorption delivers a product at the specified purity, regardless of the purity of feeding fluxes. The varied-pressure process is characterized by a higher level of productivity and lower concentration of the required substance in waste fluxes [5]. When designing the adsorption technology of oxygen production based on the TSA, the most difficult part is to calculate the coefficient of heat transfer from heating or cooling media through non-adsorbed gas located in porous bed spaces to regenerated sorbent surfaces [6]. The advantage of using temperature as a variable applied to control the process is that it is possible to reduce operating costs through harnessing waste heat from other production processes, for example from electricity generation. If waste heat is unavailable, for example if the production of oxygen is not linked with a thermal process, it is more beneficial—for economic reasons—to use varied-pressure (or temperature-controlled varied-pressure) technology.

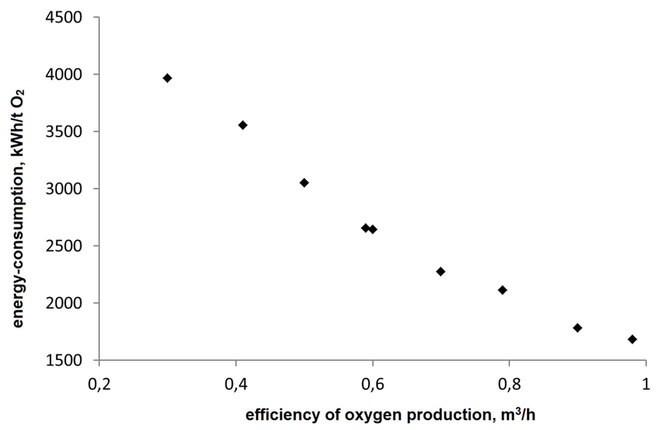


Figure 1: Dependency of energy-consumption of oxygen production (through the PSA method) on efficiency

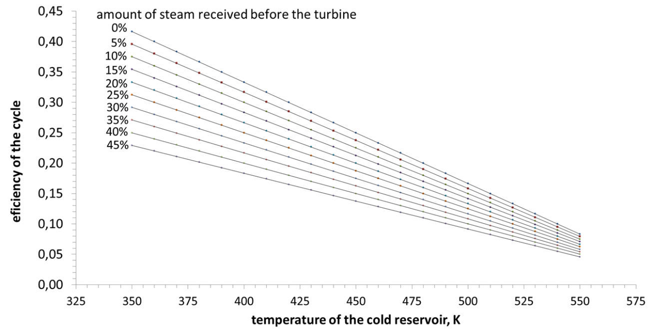


Figure 2: Carnot cycle efficiency, depending on temperatures of the cold reservoir and levels of steam received in front of turbines. Temperature of the hot reservoir: 600 K.

### *1.2. Coupling possibilities of the power plant with its oxygen station*

The thermodynamically-specified minimal operation of oxygen separation from the air is equal at 53.1 kWh/ton of oxygen. Current cryogenic installations are characterized by increasingly higher thermodynamic capabilities (still the best of them are characterized by their demand for energy exceeding minimum requirements more than three times). In the case of adsorption installations, the level of energy consumed in oxygen separation is even higher. In laboratory testing, a PSA-typed adsorption oxygen generator was examined.

Laboratory equipment specifications:

- Efficiency: up to 1 $m^3$/h
- Oxygen purity: up to 95%
- Oxygen pressure: up to 6 bar
- Continuous operation in automatic mode
- Operation in manual mode
- Two independent sets of columns with individual control systems

Fig. 1 shows the energy-consumption results obtained for oxygen production vs. efficiency of the laboratory equipment.

The studies enabled us to determine the minimum energy-consumption of oxygen production at about 1,600 kWh/$t_{O_2}$. This is a very high level of energy-consumption (even taking into account the average global energy consumption for oxygen production by all methods at 877 kWh/$t_{O_2}$).

Using the adsorption method to separate air requires energy to be supplied to adsorptive beds in the course of adsorption (the PSA, VSA methods) or heat to be supplied in the course of bed regeneration (the TSA method). Applying the second law of thermodynamics it appears that the energy supplied cannot be lower than 183.24 kJ/$kg_{O_2}$ at purity of 95%. This translates into the minimum operation of air separation at a temperature of 298.15 K. Please note that there is no technology with 100% efficiency. Several methods can be used to obtain the required amount of energy generated within thermodynamic circulations at the plant. One of them is to recover some of the produced electricity and re-use it in the process of pressure adsorption. another method is to reduce the efficiency of circulations either through an increased lower-circulation temperature or through some recovered superheated steam in front of the turbines. Thermal energy obtained in this manner can be used to separate the air through the TSA technology. Below there is a chart of reduced efficiency of the Carnot cycle depending on temperatures of the cold reservoir and on the levels of steam obtained.

An increased amount of heat provided for the purposes of air separation reduces the efficiency of electricity production. However, the larger the difference is between adsorption and desorption temperatures (thus the higher the temperature for bed regeneration), the higher the efficiency of the TSA process. The analyzes of adsorption curves available in the literature prove that—to regenerate beds—it is justified to apply temperatures just at 340 K. Further works seek to determine the efficiency of the process depending on temperature differences.

Efforts to improve the economics of oxygen production for power engineering and industry purposes require maximized utilization of all energy fluxes (including waste ones).

As the adsorption methods are dependant on both the process pressure and temperature, they can make use of various energy sources in the process of oxygen production. The PSA process, which is best described in the literature, is based on electricity. This energy is used to power-supply a compressor which maintains a high level of pressure in the course of adsorption. Another type of energy is used by the TSA process, which requires a supply of heat for use in the regeneration of adsorptive beds. These two processes of oxygen production can be combined in a method making use of both energies (PTSA).

Its main operational motive is to couple oxygen generators with a thermal engine unit, which (especially when in operation under their cogeneration regime) allows the use of both forms of energy.

On the basis of usable energy fluxes at the plant, there are various manners of coupling with the adsorption oxygen generator.

The first one is to harness some of the produced electricity from the PSA process. This is the simplest method and does not require any interference with the existing circulation of the thermal engine unit.

The second method makes use of cogeneration heat of the thermal engine unit to regenerate the adsorption beds in the TSA process. It is also possible to make use of waste heat from the power plant, but it should be noted that adsorption in this case requires heat at temperatures above 70°C so any lower temperatures would have to be raised.

These two processes can be combined so as to harness: (i) electricity for the process of adsorption and (ii) thermal energy for the process of regeneration of adsorption beds. The thermal part can be harnessed through collecting some heat at elevated temperatures and utilizing it directly to regenerate beds.

Some simplifications were made for the purposes of comparing the economics of coupling the power plant with the oxygen generator: lower and upper temperatures of the thermal circulation, power of the block and parameters of the produced product. This approach produces a measurable reference index in the form of sellable electrical power. For the purposes of simplification, this power (left to be used for oxygen production) is called net power.

Below there are some parameters to calculate energy fluxes from the power unit for the oxygen production process:

Oxygen generator:

1. Oxygen purity: 95%
2. Product flux: 350 $m^3$/h
3. Temperature of bed regeneration in the TSA and PTSA process: 90°C
4. Specific heat of zeolite: 880 J/kg/K

Table 1: Comparison of the coupling effects of the oxygen station with thermodynamic fluxes of the power plant.

| | PSA | TSA | PTSA | Cryogenics |
|---|---|---|---|---|
| Oxygen purity, % | 95 | 95 | 95 | 99 |
| Product stream, $m^3$/h | 350 | 245 | 350 | 350 |
| Net electrical power, MW | 194.8 | 178.2 | 195.1 | 199.9 |

Energy unit:

1. In order to simplify calculations—made on the Carnot cycle
2. Upper temperature: 500°C
3. Lower temperature 40°C
4. Unit power: 200 MW

After the calculations were made it was found that the quantity of usable heat with lower temperatures increased to 90°C is insufficient to reach the intended efficiency of oxygen production in the varied-temperature process. The efficiency of oxygen production obtainable for the oxygen generator in the TSA process is calculated and compared in the table below. For the purposes of comparison, Table 1also includes calculations for the cryogenic method.

In comparison with the PSA process, the PTSA processes slightly improve the economics of oxygen production. The varied-temperature adsorption method is unable to produce the required amount of oxygen under the predefined conditions.

In the present state of knowledge the cryogenic method is the most effective air separation technology. The adsorption methods may be used to consume surplus cogeneration heat at times of reduced demand by recipients.

## 2. Summary

Currently, there are three technologically advanced methods of separating oxygen from the air: cryogenic, adsorptive and membrane-based. The selection of an appropriate method of oxygen separation from atmospheric air depends on the required scale of production, purity and purity of gas waste fluxes. In the case of oxygenic combustion, the efficiency of an individual installation is the key criterion when selecting an air separation method. Assuming 500 tons of oxygen per day to be an economically reasonable threshold for the efficiency of adsorption installations, power units exceeding 25 MWe should be linked with cryogenic air-separation installations. Pilot installations, laboratory installations and oxygen combustion installations at units with minor capacities (distributed cogeneration, waste incineration plants, steelworks and others) may be supplied with oxygen from adsorption installations.

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