

7th Trondheim CCS Conference, TCCS-7, June 5-6 2013, Trondheim, Norway

## Comparative analysis of oxygen production for oxy-combustion application

Banaszkiewicz T., Chorowski M., Gizicki W.\*

*Wroclaw University of Technology, Institute of Aviation, Processing and Power Machines Engineering, Wybrzeże Wyspiańskiego 27, 50-370 Wroclaw, Poland*

---

### Abstract

Oxy-combustion is presently considered as the most promising technology to enable the capture of CO<sub>2</sub> from fossil fuel based power plants. The concept of oxy-combustion is to use oxygen instead of air for the combustion process and to achieve a high concentration of CO<sub>2</sub> in the flue gas. In this technology an exemplary 1 GWe thermal power plant will require daily about 18 000 tons of oxygen. A potential implementation of oxy-combustion on significant for power generation scale, would create the necessity of the oxygen production capacity increase by at least an order of magnitude in comparison to the present production rate. The paper categorizes the oxygen production methods and validates them with respect to oxy-combustion requirements. Present development in cryogenic air separation installations will be presented. A special attention is paid to sorption methods (TSA, PTSA) making use of heat cogenerated in thermal power plants. A novel use of high capacity heat pumps in air separation systems is proposed.

© 2013 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Selection and peer-review under responsibility of SINTEF Energi AS

Keywords: air separation, oxygen, cryogenics, TPSA, heat pump

---

### 1. Introduction

Cryogenic air separation on industrial scale started in the beginning of 20th century fostering the development of metallurgy and other branches of industry highly dependent on the availability of oxygen, nitrogen and later argon. Cryogenic air separation units (ASU) are characterized by very good quality of the products, big capacities and high reliability. In spite of other emerging technologies of air separation (sorption, membrane) cryogenics

---

\* Corresponding author. Tel.: +49 71 320 25 35; fax: +49 71 341 77 08.  
E-mail address: [wg@pwr.wroc.pl](mailto:wg@pwr.wroc.pl)

remains the basic technology for oxygen production, however restricted for the applications requiring the gases in high quantities – above several hundred tons of oxygen per day. A new challenge for air separation technologies origins from CCS policy and its consequences.

Oxy-combustion is presently considered as one of the three possible capture technologies to enable the capture of CO<sub>2</sub> from fossil fuel based power plants. A potential implementation of oxy-combustion on significant for power generation scale, would create the necessity of the oxygen production capacity increase by at least an order of magnitude in comparison to the present production rate. This requires a novel approach towards oxygen production oriented at energy consumption decrease and coupling of ASU with thermal power plants.

## 2. Oxygen separation methods for oxy-combustion purposes

The applied process and its dynamics, the achieved performance, oxygen purity, drive energy, and the quality of side products - mainly nitrogen, can create a basis for the categorization of oxygen separation methods. A summary of air separation technologies taking into account the above criteria is shown in Table 1 [3, 5, 7].

Table 1. Comparison of air separation technologies

Technology & development stage	O <sub>2</sub> purity %	Capacity, tons per day	Possible by-products, Their quality	Driving force	Start-up time
Cryogenic Matured	99 +	up to 4 000*	Nitrogen, Argon, Krypton, Xenon, Very good	Electricity	hours/days
Adsorption Matured	95 +	up to 300	Nitrogen, Bad, ca. 11% O <sub>2</sub>	Electricity Heat (70-90 °C)	minutes/hours
Membrane (polymer) Matured	~ 40	up to 20	Nitrogen Bad	Electricity	minutes
Membrane (ITM) R&D phase	99 +	laboratory scale	Nitrogen, Bad	Electricity Heat (800 °C)	hours

\* – from a single train

In case of oxygen separation for power generation purposes, in amounts closely correlated with the generation of electricity, a very important parameter is the energy consumption. In addition, it is important that the energy delivered to the separation plant may have a different character than electricity for example thermal energy. The possibility of using thermal energy allows to couple air separation unit with CHP plants, solar panels or other waste heat sources. The dynamics of the air separation unit is very important in the case of variable load power, which may be result of the large share of energy from renewable sources in the energy mix.

The right method of oxygen separation always depends on the required capacity, oxygen purity and purity of the by-products, i.e. nitrogen, argon, krypton and xenon.

The ASU's plant capacity is the main criteria in case of oxy-combustion. As shown in Table 1, cryogenic air separation units are characterized by the highest capacities, corresponding to the needs of thermal power plants. Non-cryogenic air separation methods are characterized by much lower capacities, not exceeding about 500 tons of oxygen per day in adsorption plants. Hence for oxy-combustion thermal power plants of the installed electrical capacity exceeding 25 MWe, cryogenic separation is the best method. Adsorption oxygen generators can supply

experimental plants, laboratory units and oxy-fired small capacity plants (distributed cogeneration, incineration plants, steelworks, etc.). Periodic supply of liquefied oxygen to such facilities is also possible.

### 3. Energy consumption of oxygen separation

The thermodynamic minimal work of oxygen separation from air is equal to 53.1 kWh / ton of oxygen. The best presently constructed cryogenic ASUs are characterized by energy consumption exceeding the thermodynamic minimum by about three times. Figure 1 shows a dynamics of the ASU efficiency improvement in the last 45 years. The data concern cryogenic installations only, the most efficient adsorption and membrane technologies are still characterized by the energy consumption two times higher than big cryogenic installations. The energy consumption decrease of cryogenic method is mainly due to the scale effect. The scale effect in cryogenic installations is the result of the fact that the ASU cold box capacity is proportional to its volume and the losses (mainly caused by heat transfer through the insulation) to the surface. Hence the higher the capacity is the lower the losses per unit mass of the product [1]. This effect is not to be observed in other (warm) technologies.

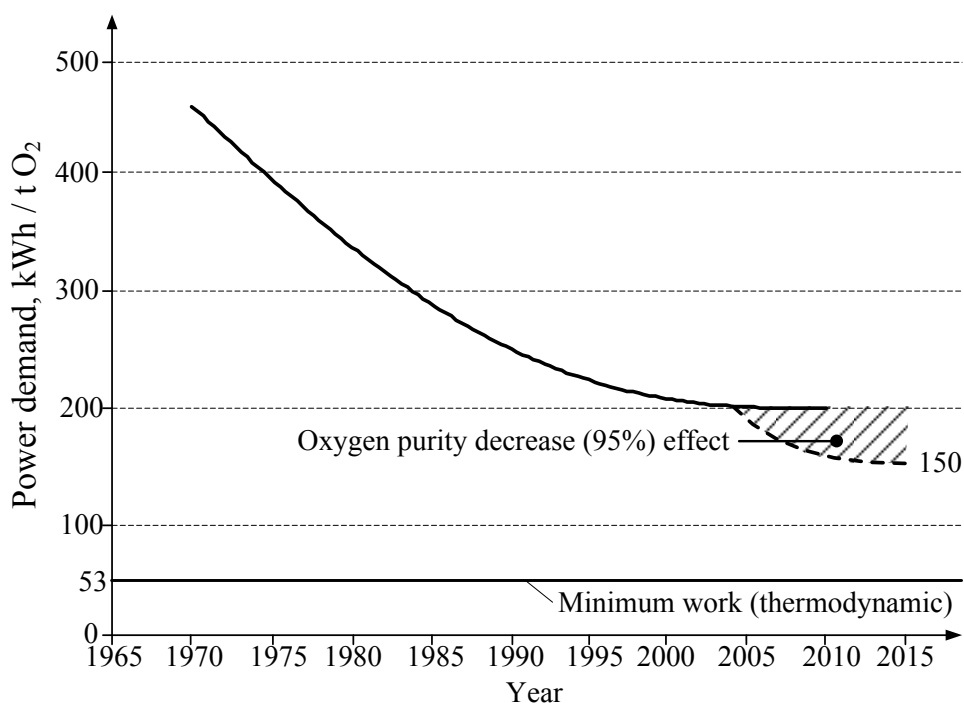


Fig. 1. Development over time of energy demand for oxygen separation [3]

Energy consumption of oxygen separation increases as a function of oxygen purity. In spite of fact that cryogenic rectification provides oxygen of a very high purity (compare Table 1), this feature is not crucial in oxy-combustion. Taking into account the energy consumption for air separation and further compression of the flue gases containing up to 90 % of CO<sub>2</sub>, an optimal oxygen purity leaving the ASU is of about 95% [2, 8]. Cryogenic installations used as ASU integrated with thermal power plants should be adapted by decreasing the oxygen quality in comparison with standard state-of-art processes. Such adaptation should lead to significant energy consumption drop. There are a number of R&D projects aimed at both oxygen purity and elementary energy consumption decrease. The oxygen purity decrease to 95% can be accompanied by energy consumption reduction of at least 10% [4,6].

Taking into account a further possible increase of cryogenic ASU capacity, and the efficiency increase resulting from the lower oxygen purity (95%), the expected energy demand per 1 ton of the separated oxygen will be of about 150 kWh/ton (540 kJ/kg). Further decrease of energy consumption is unrealistic due to the fact that the capacities of ASU single trains cannot be much increased because of transport and assembly problems. Hence the scale effect for cryogenic ASU can be considered as saturated now (Fig. 1).

In order to improve the economics of oxygen supply, the thermal connection of oxygen plant with coal-fired power or CHP plant can be considered. The waste heat can be used as a driving force in oxygen separation units.

#### **4. The use of waste heat in oxygen generation**

The integration of the air separation process with energy production in power plant can allow the use of waste heat. The use of waste heat in cryogenic installations is limited but power plants can be integrated with adsorption oxygen generation through the additional use of temperature changes in the combined pressure-temperature swing adsorption (PTSA) process.

Pressure swing adsorption (PSA) technology is well-known, matured and vastly used method of oxygen separation from the air. At relatively low energy consumption it allows to obtain sufficient purity oxygen (95%) for oxy-combustion applications at capacities up to 300 tons per day.

Swinging the temperature also can control the adsorption process, but technology based on pure temperature swing adsorption (TSA) process is not being currently developed. Waste heat can be used in a combined PTSA process that allows controlling the adsorption process more effectively. Adsorption process takes place at elevated pressure and low temperature. Regeneration of the bed occurs at low pressure and elevated temperature. Elevated temperature can be obtained by making use of waste heat from the power production process. There are three ways to connect of adsorption oxygen generator with power plant.

The first method is making use of the generated electricity for the PSA method. This is the simplest method, requires no interference with the existing power generation scheme. No use of waste heat is possible.

The second method involves the use of electricity and waste heat of cogeneration at a high temperature level (at about 90 °C) in the PTSA method.

The third method involves the use of electricity and waste heat at low temperature level (at about 40 °C) derived from the classical condensing power plant in the PTSA. The temperature of the waste heat is too low to be able to directly use in adsorption oxygen generator. In order to raise the temperature level to an appropriate value the use of a high capacity absorption heat pump is needed.

The use of an absorption heat pump allows using in the PTSA method waste heat from condensing power cycle, normally irretrievably wasted to the environment. This heat due to a low temperature at approximately 40 °C can no longer be used in any process. The use of a high capacity absorption heat pump allows to increase the waste heat stream temperature to a useful level of 90 °C. Work scheme of an absorption heat pump is shown in Figure 2.

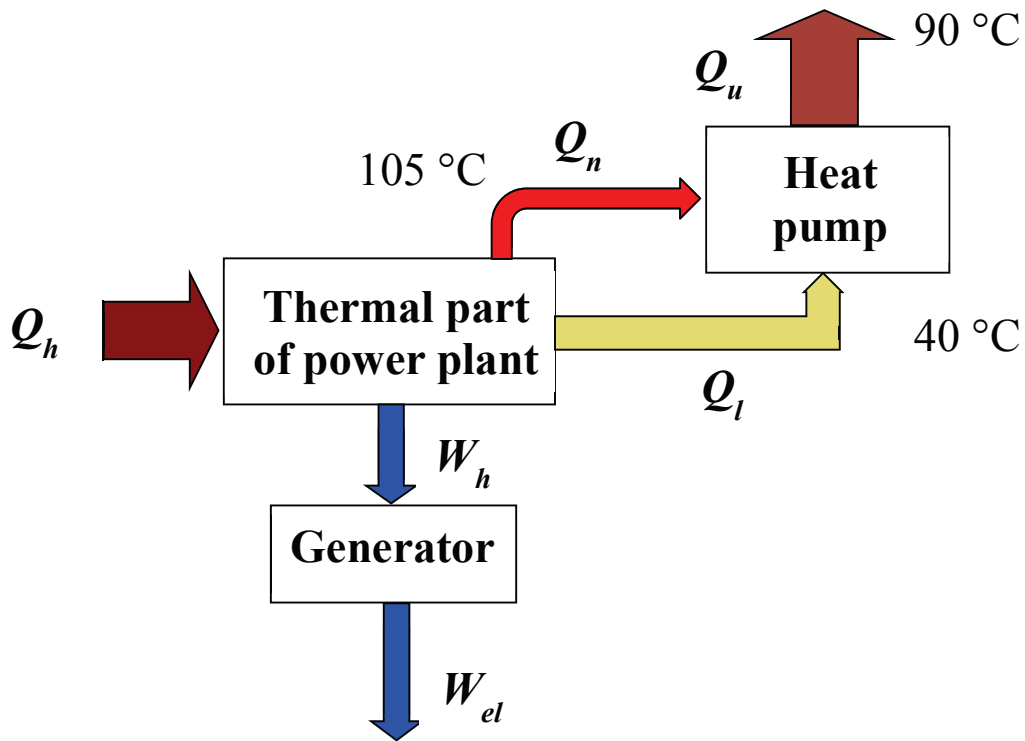


Fig. 2. Work scheme of an absorption heat pump

$Q_h$  - primary energy (high temperature level),  $W_h$  - useful work,  $W_{el}$  - electric power,  $Q_l$  - waste heat (low temperature level),  
 $Q_n$  - driving force to heat pump (steam),  $Q_u$  - waste heat (usable temperature level)

The energy flow of waste heat at a temperature of  $40\text{ }^{\circ}\text{C}$  reaches the heat pump. There, with the use of thermal compressor heat temperature is raised to  $90\text{ }^{\circ}\text{C}$ . Energy for powering the compressor is taken from the steam at a temperature of min.  $105\text{ }^{\circ}\text{C}$  coming from the turbine. The use of a heat pump is reducing the electric power production but allows the use of a waste heat at a useful temperature level. Figure 3 shows a Carnot cycle based thermodynamic model of heat pump engagement with power generation waste heat.

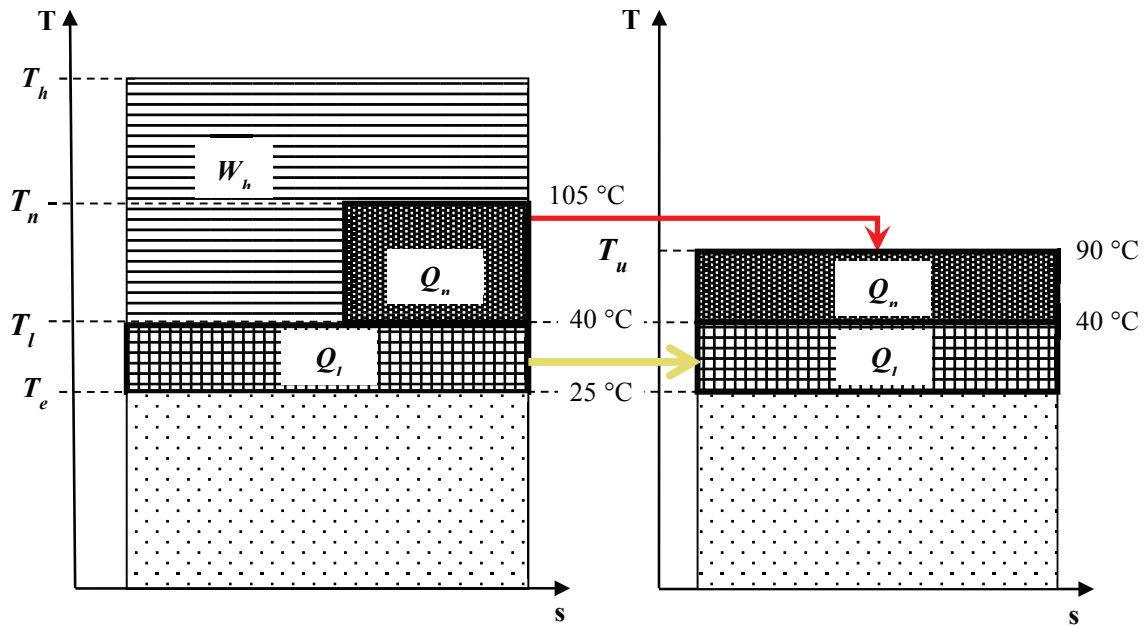


Fig. 3. Carnot cycle based thermodynamic model of heat pump integration with power generation waste heat

$T_l$  - low-level waste heat temperature,  $T_n$  - steam temperature,  $T_u$  - usable waste heat temperature

In order to estimate the economy of oxygen separation in the three methods described above the balance of electricity and heat flows, based on the Carnot model, was made. It is assumed that the power plant or CHP plant in addition to electricity generation also produces a steady stream of oxygen as a result of the adsorption-based installation (PSA or PTSA). The oxygen generation consumes only electricity (PSA) or electricity and waste heat (PTSA) from the power plant. The amount of net electricity remaining to be sold on the market after oxygen generation was compared. Other assumptions:

- Electric power of unit: 200 MW
- Upper heat source temperature: 500 °C
- Lower temperature for power plant: 40 °C
- Lower temperature for CHP plant: 90 °C
- Oxygen purity: 95%
- Oxygen flow: 350 m<sup>3</sup> / h
- Temperature of the regeneration of the bed in the PTSA: 90 °C
- Specific heat of zeolite: 880 J / (kg \* K)
- Temperatures for the heat pump as shown in Figure 2
- Heat pump COP: 6.3 (Carnot)

Results of the analysis are shown in Table 2

Tab. 2. Adsorption methods economy comparison

	PSA	PTSA	PTSA + heat pump
<b>Oxygen Purity</b>	95%	95%	95%
<b>Oxygen flow</b>	350 m <sup>3</sup> /h	350 m <sup>3</sup> /h	350 m <sup>3</sup> /h
<b>Electric Power</b>	194.8 MW	195.1 MW	197.2 MW

In comparison with the PSA process, the PTSA processes slightly improve the economics of oxygen production and at the same time allow using waste heat. Method using a high capacity absorption heat pump showed the highest efficiency of oxygen adsorption-based separation processes. Nevertheless the usage of this method causes significant increase of facility development.

## 5. Conclusions

Presently, there are three mature technologies of oxygen separation from the air: cryogenic, adsorption and polymer membrane. Oxygen obtain from polymer membranes has no sufficient purity. A choice of oxygen separation method depends on the required scale of oxygen production, its purity and the waste gases quality. In case of oxy-combustion the main criterion is plant capacity. For oxy-combustion thermal power plants of the installed electrical capacity exceeding 25 MWe, cryogenic separation is the best method. Adsorption oxygen generators can supply experimental plants, laboratory units and oxy-fired small capacity plants (distributed cogeneration, incineration plants, steelworks, etc.). High purity oxygen to the combustion oxygen is not critical. The optimum purity is about 95%. This fact allows to redesign cycles and technological schemes of currently constructed cryogenic air separation plants to reduce energy consumption by around 10%. Taking into account a further possible increase of cryogenic ASU capacity, and the efficiency increase resulting from the lower oxygen purity (95%), the expected energy demand per 1 ton of the separated oxygen will be of about 150 kWh/ton.

In order to improve the economics, the specific conditions of oxygen generation for thermal power plants should be taken into account, such as:

- reduction of the oxygen purity to 95%
- use of waste heat from power and CHP plants by using of adsorption-based PTSA process.

Applying the PTSA process in oxygen separation allows the use of waste heat from power plants. This thermal energy can be obtain directly in CHP plants at 90 °C. Even more effective is utilization of waste heat from classical condensing power plant at a temperature of 40 °C by using the heat pump performance. The heat pump allows the heat to increase the temperature up to 90 °C and its use in the process of PTSA. Analysis showed the highest efficiency of the oxygen separation using a heat pump in comparison to other methods of adsorption. Although the increase was rather marginal, the analysis in this paper shows that in some cases adding PTSA process coupled with heat pump enables the usage of waste heat to take benefit of higher energy utilization effect in cogenerated heat and power plants.

## Acknowledgments

This work has been supported by the National Centre for Research and Development, as Strategic Project PS/E/2/66420/10 “Advanced Technologies for Energy Generation: Oxy-combustion technology for PC and FBC boilers with CO<sub>2</sub> capture” and statutory funds from Ministry for Science and Higher Education (S-10057/I-2201)

## References

- [1] Chorowski M., Kriogenika - podstawy i zastosowania, IPPU MASTA, Gdańsk (2007) (in Polish)
- [2] Chorowski M., Gizicki W., Oxygen production for oxy-combustion applications, Proc. of ICEC 24-ICMC 2012, May 14-18 2012, Fukuoka, Japan, Cryogenics and Superconductivity Society of Japan (2013)
- [3] Chorowski M., Gizicki W., Gromada M., Nowak W.(red.), Czakiert T (red.), Spalanie tlenowe dla kotłów pyłowych i fluidalnych zintegrowanych z wychwytem CO<sub>2</sub>, rozdział 10: Produkcja tlenu na potrzeby spalania tlenowego, Wydawnictwo Politechniki Częstochowskiej, Częstochowa, (2012) (in Polish)
- [4] Fu C., Gundersen T., Optimized Air Separation Units for Oxy-Combustion Processes, Proc. of the 23rd IIR International Congress of Refrigeration, Prague, Czech Republic, August 21 - 26 (2011)
- [5] Franco, F., Bolland, O., Booth, N., Macchi, E., Manzolini, G., Naqvi, R., Pfeffer, A., Rezvani, S., Zara, M.A., D 4.6 Common Framework Definition Document, [http://caesar.ecn.nl/fileadmin/caesar/user/documents/D4.6-Common\\_Framework-final.pdf](http://caesar.ecn.nl/fileadmin/caesar/user/documents/D4.6-Common_Framework-final.pdf) (2009)
- [6] Prosser N., Shah M., Air Separation for Oxy-coal Power Plants, Proc. of the 2<sup>nd</sup> Oxyfuel Combustion Conference, Queensland, Australia, September 12 - 16 (2011)
- [7] Smith A.R., Klosek J., A review of air separation technologies and their integration with energy conversion processes, Fuel Processing Technology (2001), Vol. 70, pp. 115-134
- [8] Wilkinson M. B., Boden J. C., Panesar R. S., Babcock M., Allam R. J., CO<sub>2</sub> Capture via Oxyfuel Firing: Optimisation of a Retrofit Design Concept for a Refinery Power Station Boiler, First national Conference on Carbon Sequestration, Washington DC, USA, May 15-17 (2001)