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Comparative Analysis of Cryogenic and PTSA Technologies for Systems of Oxygen Production

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Abstract. Development of oxy-combustion technology requires relatively lower purity oxygen production (90 - 95% O_2). There are two known methods to produce oxygen in such purity level – cryogenic and sorption. Cryogenic air separation technology is currently well developed and widely used for oxygen production in large quantities (up to 5 000 tons per day from a single technology train). The second method is pressure swing adsorption (PSA), which is well suited for smaller quantities of oxygen (below 500 tons per day). To optimize overall energy consumption, the PSA method can be combined with swing of temperature by using waste heat from combined heat-power generation (cogeneration) processes, leading to pressure temperature swing adsorption (PTSA). In small and medium scale oxygen production systems for oxy-combustion, both PTSA and cryogenic method can be used. The paper shows calculations and experimental validation of the efficiency and economics for both processes. The limitations of applicability for each of these technologies are indicated. The possibility of coupling the technologies, including thermal power plants, in order to improve the efficiency of the oxygen separation is discussed.

Keywords: air separation, oxygen, cryogenics, PTSA, heat pump.
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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 finally argon. Cryogenic air separation units (ASU) are characterized by very good quality of the products, big capacities and high reliabilities. In spite of other emerging technologies of air separation (sorption, membrane), cryogenics remains the basic technology for oxygen production. However, cryogenics are restricted for the applications requiring the gases in high quantities – above several hundred tons of the separated gases per day. Oxy-combustion is the most promising high capacity and relatively matured method of CO_2 originating from thermal power plants sequestration. Oxy-combustion is the process of burning a fuel using pure oxygen, or oxygen enriched air, instead of atmospheric air, as the primary oxidant. Oxy-combustion is now considered the most prospective technology to be implemented on a mass scale in thermal power plants. That is because it allows a high concentration of CO_2 in the flue gas, thus enabling its direct sequestration. A potential implementation of oxy-combustion on significant for power generation scale, would create the demand for oxygen on unprecedented scale in comparison to the present production rate. A thermal power plant of 1 GWe electrical power would require of about 18 000 tons of pure oxygen per day. Hence, a potential implementation of Carbon Capture and Storage (CCS) policy may create a demand for oxygen exceeding present production rate by two orders of magnitude. It is also a fact that the purity of the oxygen used as the primary oxidant in oxy-combustion installations is not critical. The oxygen can comprise up to about 5% of impurities, mostly nitrogen and argon. This content of impurities results from the complex optimization of air separation and CO_2 compression prior to storage. This condition allows the use of oxygen separated in sorption processes allowing to achieve the oxygen of 95% purity. This requires a novel approach towards oxygen production oriented at energy consumption decrease and energy coupling of ASU with thermal power plants.

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.

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TABLE 1. Comparison of air separation technologies

Technology & development stage	O_2 purity %	Capacity, tons per day	Possible by-products, Quality	Energy demand kWh/ton O_2	Driving force	Start-up time
Cryogenic Matured	99 +	up to 4 000*	Nitrogen, Argon, Krypton, Xenon, Very good	200(1)	Electricity	hours/ days
Adsorption Matured	95 +	up to 300	Nitrogen, Bad, ca. 11% O_2	500(2)	Electricity Heat (70-90 °C)	minutes/ hours
Membrane (polymer) Matured	~ 40	up to 20	Nitrogen, Bad	–(4)	Electricity	minutes
Membrane (ITM) R&D phase	99 +	laboratory scale	Nitrogen, Bad	400(3)	Electricity Heat (800 °C)	hours

* – from a single train
(1) – data from existing installations,
(2) – laboratory-based estimation,
(3) – literature data,
(4) – not applicable due to low oxygen purity

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 per unit amount of separated oxygen. In addition, it is important that the energy delivered to the separation plant may have a different character than electricity, such as thermal energy. The possibility of using thermal energy allows coupling an 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 the 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 having 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 (e.g. distributed cogeneration, incineration plants, steelworks, etc.). Periodic supply of such facilities by liquefied oxygen is also possible.

In some cases, the capacities of ASU installations may purposely exceed the instantaneous demand from thermal power plants for oxygen. It would enable the oxygen production when the excess electricity is available by storing energy in the form of liquid or compressed gases. The highest potential for energy storage have cryogenic installations due to high density of liquefied gases. Both oxygen and nitrogen can be used later as chemicals or physical exergy carriers. Compressed gases can also be used as energy reservoirs, but the potential for such applications of non-cryogenic air separation installations is low. In case of sorption systems, only one gas (oxygen) is delivered at elevated pressure in the order of several bars. Highly contaminated nitrogen is relieved to the environment under pressures close to atmospheric. The advantage of sorption PTSA plants is their ability of making use of relatively low temperature heat sources and conversion of heat exergy to the exergy of warm compressed oxygen. However the estimated exergy efficiency of such conversion is below 20%.

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 the dynamics of the ASU efficiency improvement in the last 45 years. The decrease in specific power consumption is highly correlated to the growth of cryogenic installations capacities – Figure 2. 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 the cryogenic method is mainly due to the scale effect. The scale effect in cryogenic installations is the result of 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.

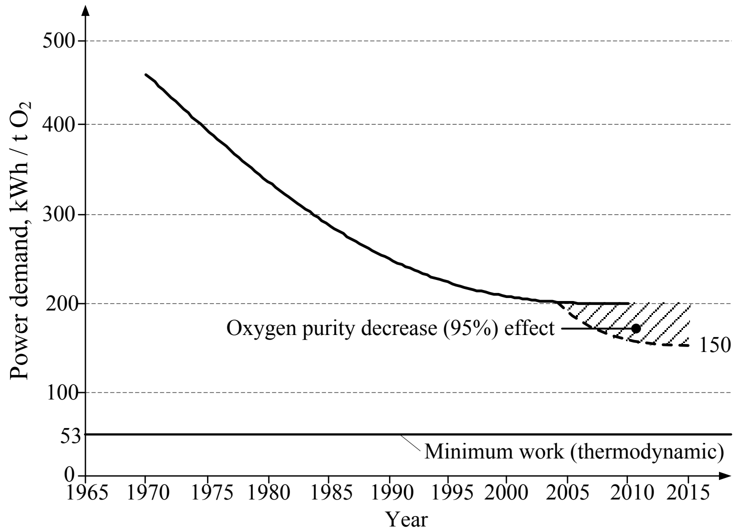

FIGURE 1. Dynamics of energy demand for oxygen separation decrease [3]

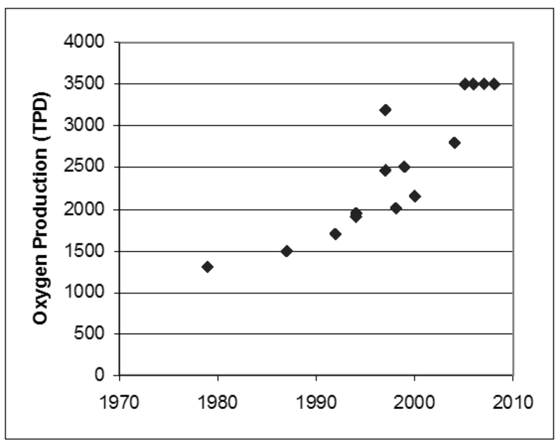

FIGURE 2. Cryogenic air separation units capacity increase (single train) [3]

Energy consumption of oxygen separation is an increasing function of oxygen purity. In spite of the 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_2, an optimal oxygen purity leaving the ASU is about 95% [2]. 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% [4,5].

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 about 150 kWh/ton (540 kJ/kg). Further decrease of energy consumption is unrealistic due to the capacities of ASU single trains cannot be increased much 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 coupling of oxygen plant with coal-fired power or CHP plant can be considered. The waste heat as a driving force can be used from cogeneration and from power plant as well.

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 swings in a combined pressure-temperature process (PTSA).

Pressure swing adsorption technology (PSA) is well-known, matured and a vastly used method of oxygen separation from the air. At relatively low energy consumption, it can obtain sufficient purity oxygen (95%) for oxy-combustion applications at capacities up to about 300 tons per day. This reduction of adsorption system performance results from the competitiveness of cryogenic installations above this value.

Swinging the temperature also can control the adsorption process, but technology based on pure TSA process is not currently being developed. Waste heat can be used in a combined pressure-temperature swing process (PTSA) 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 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 and 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 from 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 use directly in an 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 fourth concept would be coupling the cryogenic ASU installation with PTSA. Namely the heat recovered from the high capacity air compressors can be used for regeneration of the adsorption beds. To raise the temperature of the heat rejected from the compressors, a heat pump can be considered as well.

USE OF ABSORPTION HEAT PUMP IN SORPTION AIR SEPARATION

The use of an absorption heat pump in the PTSA method allows the use of waste heat from condensing power cycle, that normally is wasted to the environment. This heat due to a low temperature at approximately 40 °C is characterized by practically zero exergy and cannot be directly transformed into an other form of energy. In the case of big thermal power plants, the condensers create a stable low temperature heat source which can be further upgraded with a use of a heat pump. The use of a high capacity absorption heat pump allows increasing the waste heat stream temperature to a useful level of 90 °C. The process scheme of an absorption heat pump is shown in Figure 3.

The energy flow of waste heat at a temperature of 40 °C reaches the heat pump. There, with the use of a thermal compressor, heat temperature is raised to 90 °C. Energy for powering the compressor is taken from the steam at a temperature of min. 105 °C coming from the turbine. The use of a heat pump reduces the electric power production but allows the use of a waste heat at a useful temperature level. An example of a heat pump application at a thermal power plant is shown in Fig. 4. The heating power at the heat station is generated not in direct cogeneration but in the absorption heat pump, reducing the use of 95 °C condensate. In our concept, the heat station will be replaced by an adsorption bed requiring heat for regeneration.

In order to make a comparison of the oxygen separation using the three sorption related 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 heat (PTSA), from the power plant. The amount of net electricity remaining for distribution after oxygen generation was compared. Other assumptions taken for calculations are:

- Electric power of unit: 200 MW
- Upper Temperature: 500 ºC
- Lower temperature for power plant: 40 °C
- Lower temperature for CHP plant: 90 °C
- Oxygen purity: 95%
- Oxygen flow: 350 m^3 / 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)

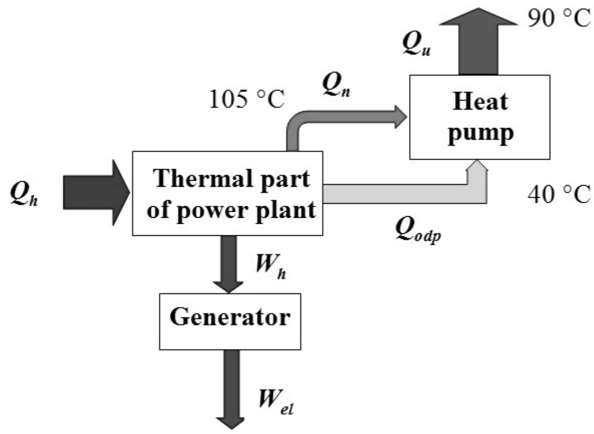

FIGURE 3. Work scheme of an absorption heat pump
Q_h - primary energy, W_h - useful work, W_{el} - electric power, Q_{odp} - waste heat (low level), Q_n - driving force to heat pump (steam), Q_u - waste heat (high level)

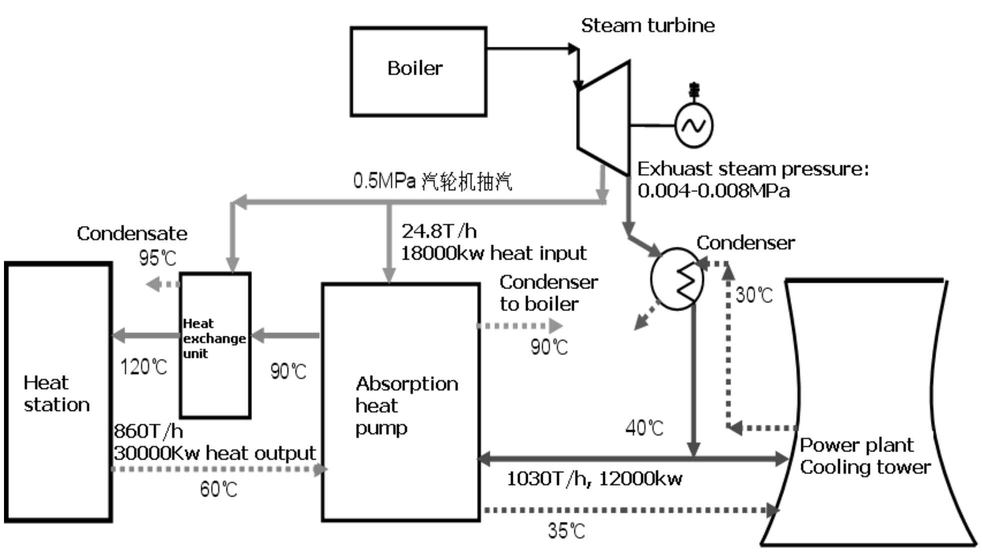

FIGURE 4. Application of heat pump at Guoyang New Energy

Results of the analysis are shown in Table 2, the data for cryogenic method were calculated assuming energy requirement of 150 kWh/ton of separated oxygen – compare Figure 1.

TABLE (2). Adsorption methods economic comparison

	PSA	PTSA	PTSA + heat pump	CRYOGENIC (for reference)
Oxygen Purity	95%	95%	95%	95%
Oxygen flow	350 m^3/h	350 m^3/h	350 m^3/h	350 m3/h
Electric Power	194.8 MW	195.1 MW	197.2 MW	199.9 MW

Cryogenic air separation is the most energy efficient for high fluxes of oxygen. However, sorption methods are competitive for lower capacities. In comparison with the PSA process, the PTSA processes slightly improve the economics of oxygen production while using waste heat. The method using a high capacity absorption heat pump showed the highest efficiency of oxygen adsorption-based separation processes.

CONCLUSIONS

Presently, there are three mature technologies of oxygen separation from the air: cryogenic, adsorption and polymer membrane. Oxygen obtained 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 with 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.). The optimal purity of oxygen for oxy-combustion is about 95%. This fact allows one 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. Other possibility of improvement the efficiency of the process is the use of waste heat from power and CHP plants, through use 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 the utilization of waste heat from classical condensing power plants at a temperature of 40 °C by using absorption heat pumps. The heat pump allows the heat to increase the temperature up to 90 °C and is used in the process of PTSA. Analysis showed the highest efficiency of oxygen separation uses a heat pump in comparison to other methods of adsorption.

An interesting option is coupling cryogenic air separation with sorption methods via the recovery of heat of compressors from cryogenic ASU and use it for adsorption beds regeneration.

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