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Technology of oxygen production in the membrane-cryogenic air separation system for a 600 MW oxy-type pulverized bed boiler

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Abstract In this paper the results of the thermodynamic analysis of the oxy-combustion type pulverized bed boiler integrated with a hybrid, membrane-cryogenic oxygen separation installation are presented. For the calculations a 600 MW boiler with live steam parameters at 31.1 MPa /654.9 °C and reheated steam at 6.15 MPa/672.4 °C was chosen. In this paper the hybrid membrane-cryogenic technology as oxygen production unit for pulverized bed boiler was proposed. Such an installation consists of a membrane module and two cryogenic distillation columns. Models of these installations were built in the Aspen software. The energy intensity of the oxygen production process in the hybrid system was compared with the cryogenic technology. The analysis of the influence of membrane surface area on the energy intensity of the process of air separation as well as the influence of oxygen concentration at the inlet to the cryogenic installation on the energy intensity of a hybrid unit was performed.

Keywords: Oxygen production; Membrane air separation; Cryogenic air separation

1 Introduction

Electricity, both in Poland and in the world, is generated most frequently in power plants powered by fossil fuels. In the European Union the share

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of electricity produced from burning such fuels as coal and natural gas is over 50%, whereas in Poland it is over 90% [1,2]. Technologies based on coal combustion emit significant quantities of CO_2 into the atmosphere – constituting to about 34% of global emissions. Therefore, in order to reduce the harmful effect of this gas, the EU introduced legislation in the form of emissions trading system [3,4]. In XXI century development of coal power engineering is directed towards the necessity of limitation of carbon dioxide emissions, thus, also towards searching for new technologies for low-energy intensive CO_2 capture. One of the methods allowing to reduce carbon dioxide emissions is oxy-combustion technology, which involves burning of fuels in an oxygen-enriched atmosphere. The resulting flue gases in this system consist mainly of carbon dioxide and water vapor. At present, oxygen production technology for oxy-combustion type boilers uses usually cryogenic air distillation. The energy intensity of such systems is at the level of 0.22–0.34 kWh/kgO_2 [5]. However, oxygen can also be produced by other methods, e.g. in the adsorption and absorption process or with the use of low- and high-temperature membranes [6]. In this paper an oxygen separation method with the use of hybrid membrane-cryogenic system was proposed, in which as the first stage a polymer membrane is used and the second stage consist in a double cryogenic distillation column.

2 Main assumption for the calculations

One of the most energy consuming process in the oxy-combustion technology of electricity generation is production of oxygen. The most frequently used technology for oxygen production is based on the cryogenic process. However, it is very energy consuming. An alternative can be a technology based on membranes. The main disadvantage of the existing low-temperature membranes is low efficiency of the oxygen production, i.e. low purity of the oxygen produced and its low recovery rate.

2.1 The characteristics of the pulverized boiler working in oxy-combustion technology

The thermodynamic analysis of the pulverized bed boiler designed for a 600 MW$_e$ power plant, with live steam parameters at 650 °C/31.1 MPa and reheated steam parameters 670 °C/6.15 MPa, integrated with hybrid membrane-cryogenic oxygen separation plant was performed. It was as-

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sumed that the supplied coal is composed of: carbon – 0.6125, sulfur – 0.0110, hydrogen – 0.0390, nitrogen – 0.0093, oxygen – 0.0650, moisture – 0.1732, ash –0.0900. Coal, before supplying to the furnace chamber is grinded in the coal mill. Model of the pulverized boiler consists of furnace chamber (FC), evaporator (EVAP), primary (PH) and secondary (SH) heater. Flue gas stream transfers the heat in the economizer (ECO), recirculated flue gas heater (RFGH) and oxidant heater (OH). The flue gas cleaning section consists of such elements as electrostatic precipitator (EP), exhaust fan, flue gas cooler (FGC), desulphurization installation (DSI) and flue gas dryer (FGD). Oxidant for the combustion process is produced in the air separation unit (ASU). Scheme of the boiler is presented in Fig. 1.

Basic operation parameters of the boiler are as follow: life steam pressure/temperature 31.1 MPa/654.9 °C, reheated steam pressure/temperature 6.15 MPa/672.4 °C, oxidant excess ratio 1.2, oxygen share in the mixture of recirculated flue gas/oxygen from ASU supplied to the combustion chamber 30%, composition of the oxidant from ASU: 95% O_2, 5% N_2.

2.2 Membrane air separation method

The process of gas separation in the membrane technology consists in the use of a solubility-diffusion mechanism, which assumes that the components penetrating through the membrane dissolve and diffuse along the pressure gradient. The feed stream is separated by the membrane onto two streams, namely permeate and retentate. The permeate is enriched in the component separated by the membrane, the retentate is left before the membrane, enriched in the component retained on the membrane. A scheme of the membrane separation process is shown in Fig. 2.

The driving force of the separation process is caused by a vacuum pump used on the permeate side. The resulting product stream (J_i) depends on a membrane permeability (P_i), thickness (x), surface area (A_m) and components partial pressure difference on both sides of the membrane, i.e. on the feed side ($p_F X_i$) and permeate side ($p_P Y_i$). It can be determined from the relation:

$$dJ_i = \frac{P_i}{x}(p_F X_i - p_P Y_i)dA_m \; . \qquad (1)$$

2.3 Cryogenic air separation method

Cryogenic separation is currently the only commercially fully mature technology for oxygen production in the large scale. It uses multiple columns

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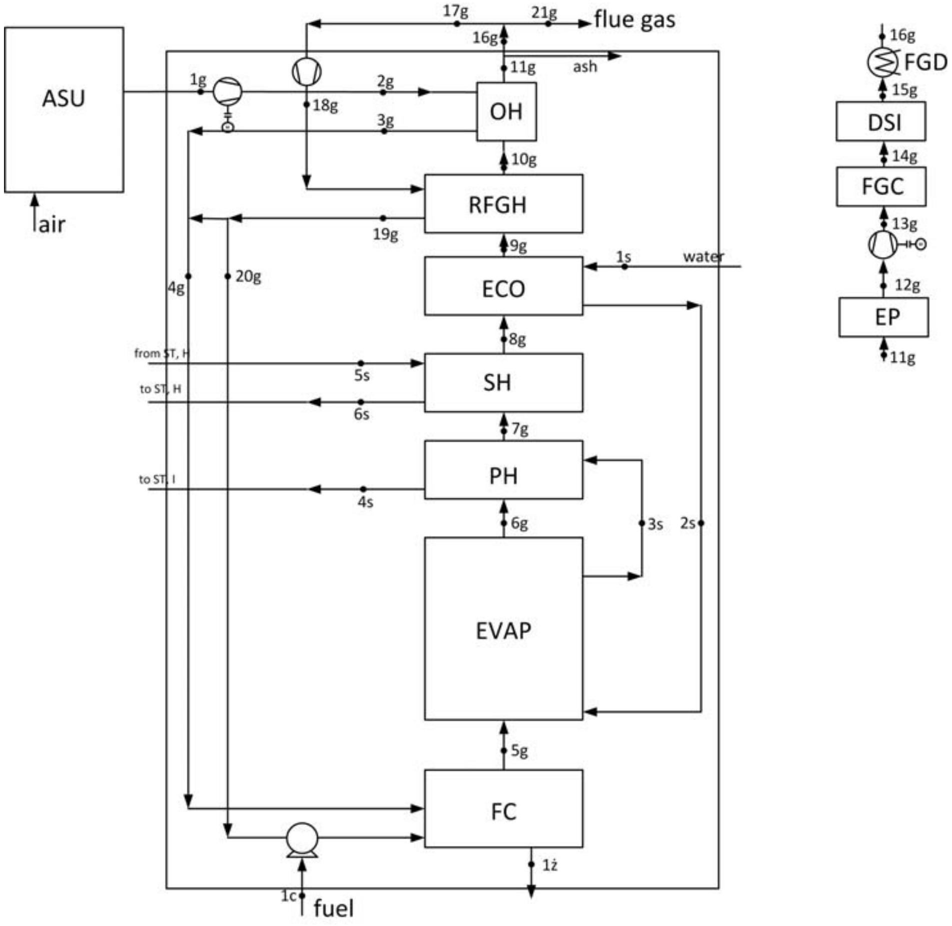

Figure 1. Structure of the pulverized boiler modeled in the analysis.

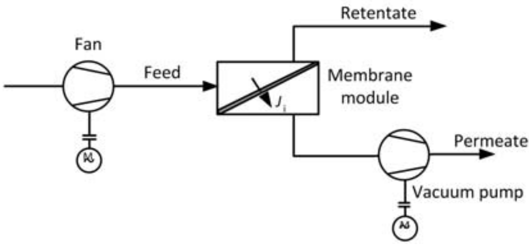

Figure 2. Scheme of membrane air separation.

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(usually two) cryogenic distillation process (carried out at cryogenic temperatures) to obtain high purity oxygen. Cryogenic separation of mixtures uses the difference in boiling points of the mixture components.

The most energy intensive components of an oxygen plant are air compressors. In order to reduce the compression work, usually multistage compressors with interstage cooling are used. Energy consumption of the cryogenic separation process of oxygen from air also depends on the purity of the resulting oxygen. The theoretical energy requirement is 0.07 kWh/m_n^3 but in practice it is much higher and reaches a value between 0.32–0.35 kWh/m_n^3 (for purity at 99.5%) and 0.336 kWh/m_n^3 (for purity at 95%) [7,8]. Recalculating on 1 kg of separated oxygen in [9] a demand of 0.269 kWh/kgO_2 is reported and in [8] of 0.219 kWh/kgO_2 for the stream of oxygen at the purity of 95%. A detailed description of the a cryogenic separation installation can be found, among others, in [7,10–12].

3 Analysis of the hybrid membrane cryogenic air separation technology

In the calculations presented in this paper it was assumed that the oxidant directed to the oxy-combustion boiler is produced in the hybrid membrane-cryogenic module. The hybrid membrane-cryogenic technology consists of the membrane module and two cryogenic distillation columns section. In the cryogenic installation compression of the air supplied to the columns requires high amount of electricity. In the hybrid installation the stream of air with higher concentration of oxygen is directed to the cryogenic column. It can cause a reduction of the energy intensity of compressors in the cryogenic module and, consequently, of the whole oxygen plant. Scheme of the analyzed hybrid installation is shown in Fig. 3.

Calculations of the membrane oxygen separation installation was made in the Aspen Custom Modeler 2004 [13]. The membrane made of phenolic resin material with permeability coefficient for O_2 equal to 3.1119 m_n^3/m^2hbar and for N_2 equal to 0.2922 m_n^3/m^2hbar and selectivity coefficient $\alpha = 10.6$ was chosen [14]. It was assumed that the air is directed to the membrane by a fan, where the pressure increase is 0.05 bar. Underpressure behind the membrane is created by a one-section vacuum pump.

In order to conduct the analysis a model of a cryogenic air separation plant was built in the commercial Aspen Plus package. In the calculations a real gas model PENG-ROB was used, worked out by Peng and Robinson

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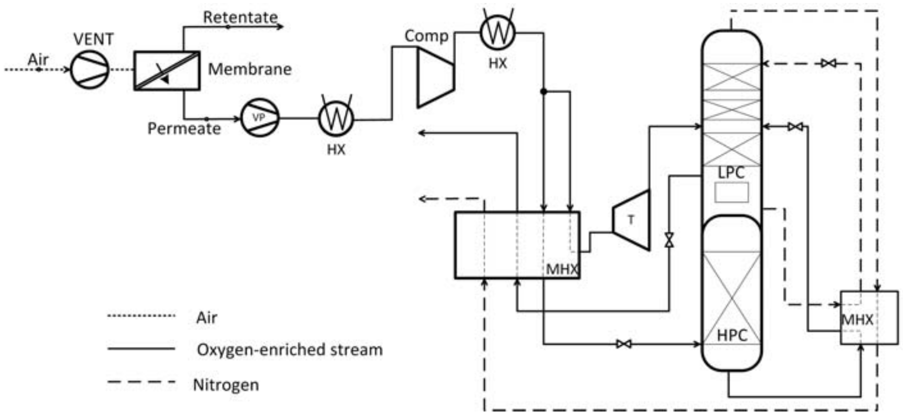

Figure 3. Scheme of a hybrid membrane-cryogenic oxygen production installation (HX – heat exchanger, VOI – vaccum pump, T – turbine).

[15]. In the model it was assumed that the compressor of the air supplied from the membrane installation is a four-sections machine with the inter-stage cooling to 30 °C. The pressure ratios of each section are equal and the isentropic efficiency was assumed at the level of 0.9. The air is compressed in a compressor (Comp) to the pressure of 1 bar higher than required in a high-pressure distillation column (HPC), i.e. to 6 bar. Air is first cooled in a water cooler and next further cooled in multi-stream heaters (MHX), thanks to the heat taken from the cold final products of separation (oxygen and nitrogen) and due to the expansion work in the valves. The effect is partial liquefaction of the air, which is then split in the distillation columns (HPC and LPC) into nitrogen and oxygen. In the model it was assumed, that gaseous products are obtained, at the temperature and pressure close to the ambient. In such a way, a reference energy intensity of the cryogenic installation was determined and is equal to 0.223 kWh/kgO_2.

As a result of the analysis of the boiler the stream of oxidant needed to obtain the required power was calculated. Cryogenic distillation section has to produce oxygen stream equal to 111.4 kg/s, with the oxygen concentration at 95%. In the first step of the analysis, for the the cryogenic column, the influence of the oxygen concentration on the required feed stream was investigated. Figure 4 shows the results of the obtained values of the feed stream needed for cryogenic section as a function of the concentration of oxygen in the air suplied to this section.

Oxygen concentration in the air was changed between 21 and 50%. With

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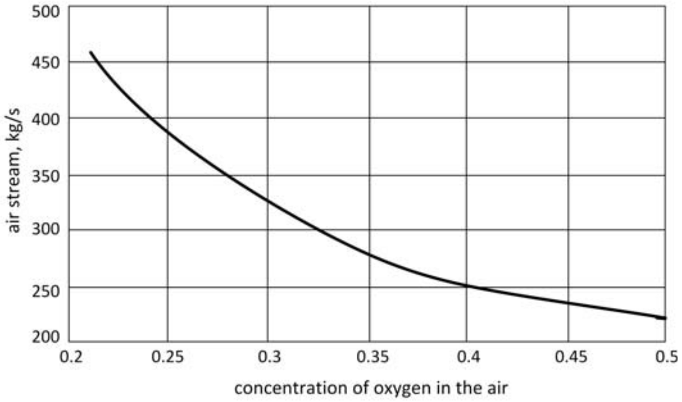

Figure 4. The dependence of the required air stream for cryogenic module on the oxygen concentration in the air.

the increase of the oxygen concentration the required air stream supplied to the cryogenic module decreases. This stream is minimal and obtains a value of 220.112 kg/s for oxygen concentration equal to 50%, while the maximum stream is 456.7 kg/s for pure air.

In order to calculate the air stream at required for cryogenic distillation section parameters, the membrane module was analyzed in details. An important parameter during the calculations is energy intensity of the air separation process. Energy intensity of a membrane module (E_{MEM}) is expressed in kWh/kgO_2 and can be determined as

$$E_{MEM} = \frac{N_{el,VENT} + N_{el,VP}}{n_p(Y_{O_2})M_{O_2}} \;, \tag{2}$$

where:

$N_{el,VENT}$ – electric power required to drive the fan, kW

$N_{el,VP}$ – electric power required to drive the vacuum pump, kW

n_P – permeate molar stream, kmol/s

Y_{O2} – oxygen concentration in the permeate,

M_{O2} – oxygen molar mass, kg/kmol.

In order to determine a minimum of the energy intensity when performing calculations of the membrane model, constant parameters of the obtained stream and permeate purity were assumed, while as variables membrane surface area and pressure of permeate were treated. The obtained results are presented in Fig. 5.

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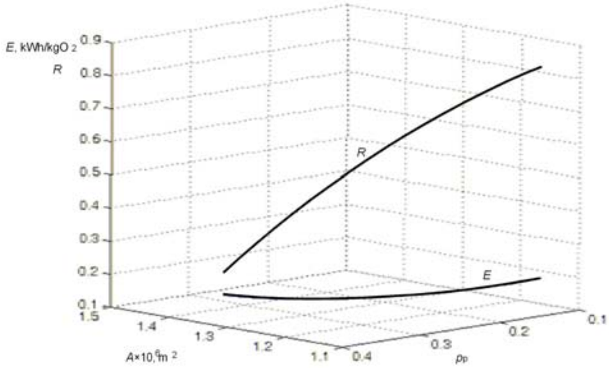

Figure 5. The dependence of the energy intensity (E) of the air separation process in the membrane module and oxygen recovery rate (R) on the membrane surface (A) and permeate pressure (p_p) for oxygen concentration in the permeate equal to 50%.

Permeate pressure was changed in the range from 0.10 to 0.29 bar and membrane surface area from 1.166 mln m^2 to 1.450 mln m^2. Oxygen recovery rate (R) is a decreasing function with the increase of the surface area (A) and permeate negative pressure (p_p), and changes in the range between 0.81 and 0.18. Energy intensity of the membrane separation process reaches a minimum equal to 0.103 kWh/kgO_2 for the point at parameters $R = 0.33$ and $A = 1.399 \times 10^6 m^2$. For the purpose of optimization of the oxygen production installation the analogical analysis was performed for each of the supply stream of the membrane module in the range of oxygen concentration 0.22–0.50.

Similarly as in the case of the membrane module, the energy intensity of the cryogenic installation (E_{CRYO}) was calculated from the formula

$$E_{CRYO} = \frac{N_{el,COMP}}{n_{O_2}(Y_{O_2})M_{O_2}} \tag{3}$$

where $N_{el,COMP}$ is the electric power needed to drive the compressor with n-sections and n_{O_2} is the molar stream of oxygen. In Fig. 6 the energy intensity of the cryogenic module as a function of the amount of compression sections is presented, for the share of oxidant at the inlet equal to 50% and the temperature 30 °C.

It results from the analysis, that the use of a four-section compressor in comparison to a single-section one allows for the energy saving at 18%.

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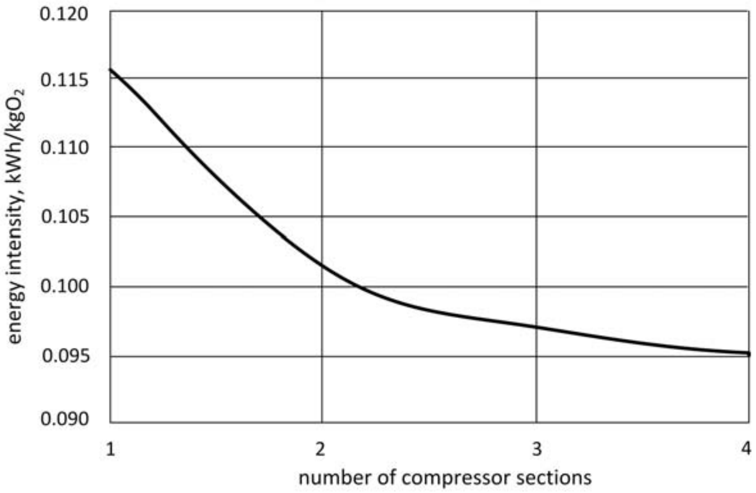

Figure 6. Energy demand of the cryogenic module as a function of a number of compressor's sections.

Thus, in further calculations it was assumed, that in the cryogenic module a 4-section compressor operates.

In the last stage of the analyses the total energy demand of a hybrid installation was calculated. It was compared with the energy intensity of the reference cryogenic installation producing oxygen from the atmospheric air. In Fig. 7 energy intensities of the cryogenic installation, membrane module and hybrid installation are presented. In the membrane module minimum energy intensity for the share of oxygen in the permeate in the range 0.22–0.50 was calculated (as shown in Fig. 6). Total energy demand of the hybrid technology was determined as a sum of the energy demands of the membrane and cryogenic installation. It results from the graph, that the energy intensity of the membrane installation is an increasing function together with the increase of the oxygen concentration in the permeate, while the energy intensity of a cryogenic installation is a decreasing function. The figure also shows the energy demand of air ventilator and of the vacuum pump in the membrane module. The energy intensity of the hybrid technology reaches minimum for the oxygen concentration equal to 49% and is equal 0.198 kWh/kgO_2, which is 12.4% lower than the reference value (for the cryogenic installation).

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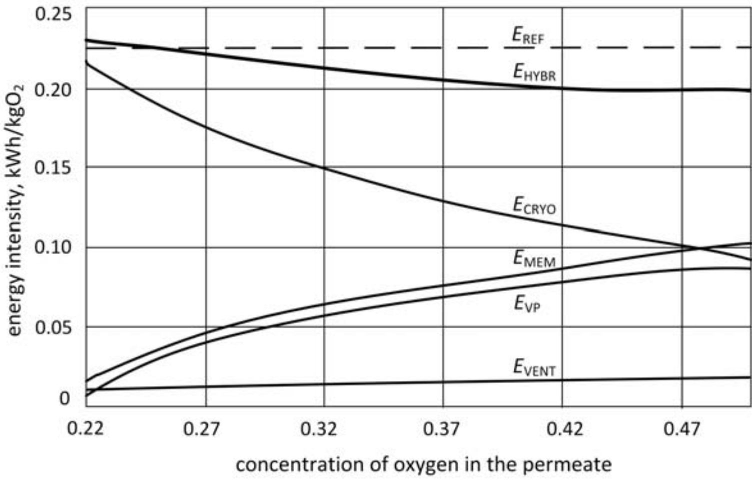

Figure 7. Energy intensity of the process as a function of oxygen concentration in permeate.

4 Summary and conclusions

In the work presented in this paper the analysis of a hybrid membrane-cryogenic installation for oxygen production for a pulverized-coal boiler working in the oxy-technology producing steam for the case of a 600 MW_e power plant was made. In the hybrid module oxygen with the purity of 95% was produced. In the currently operating for the energy installations cryogenic installations the concentration of oxygen at the inlet to the system is 21%. In the conducted research the concentration of oxygen was increased in the range between 22% and 50% and the influence of such an increase on the operation of distillation columns was analyzed. Increased concentration of oxygen in the air is realized with the use of membrane module. After conducted calculations it can be stated that the stream of air to the cryogenic installation decreases with an increase of oxygen in the feed, which translates into lower energy intensity of the distillation process in the cryogenic module. For the considered concentrations of the feed stream of the cryogenic installation, membrane surface area and permeate pressure were selected in such a way to obtain the lowest energy intensity of the process. As a result the value of 0.198 kWh/kgO$_2$ was obtained, thus a value 12.4% lower than for the reference case, i.e. cryogenic installation supplied by the atmospheric air. Such results were obtained for the following parameters:

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membrane surface equal to 1.478 mln m^2 and permeate pressure equal to 0.28 bar. Concluding, it can be stated that the hybrid membrane-cryogenic installation can be an alternative to the currently used cryogenic processes with respect to the auxiliary power of the installation. Further research including economic analysis will be conducted by the authors.

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