

ENERGETIC AND EXERGETIC ANALYSIS OF OXYGEN-ENHANCED COMBUSTION PROCESSES

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Abstract. This paper presents an energetic and exergetic analysis of application of oxygen-enhanced combustion (OEC) processes in unpressurized furnaces. The main components of combustion system are modeled, in addition to the air separation unit, which consists of polymeric membranes. Results show an increase of the energetic efficiency, from 22% to 58%, in respect to regular atmospheric combustion. The exergetic efficiency follows the same trend, from 18% to 48.5%. A reduction of more than 60% of specific pollutants emissions is shown. The assessed technique points out to be energetically more attractive than cryogenics for small plants, the size limit depending on operating conditions.

Keywords: Oxygen-Enhanced Combustion, polymeric membranes, energetic and exergetic analysis

1. INTRODUCTION

Oxygen-Enhanced Combustion (OEC) can be seen as an intermediate process between the regular atmospheric combustion and oxy-fuel combustion. The former uses air as its oxidant stream, which is abundant and cheap, but carries around 79% of its concentration in N_2 , lowering the potential energetic availability of the fuel and causes pollution due to nitrogen reaction. Oxy-fuel combustion eliminates N_2 by injecting pure O_2 in the oxidant feed, blended to recirculate CO_2 , a costly operation, limiting plant sizes to large scales and highly integrated projects. OEC is a process that operates with lower N_2 content in the feed stream, and can be placed in the middle way if compared to previously discussed combustion systems. OEC can allow an increase of the process thermal efficiency, a reduction of fuel consumption, a reduction of flue gases volumes and/or a reduction of pollutant emissions (Baukal, 1998), compared to the conventional combustion of any kind of fuel.

Together with Oxy-fuel combustion, one of OEC major costs lies on oxygen generation. Nevertheless, technologies differ from each other because OEC can operate with streams with less N_2 than in the atmospheric composition one, i.e., highly concentrated in O_2 , when oxy-fueled systems need pure O_2 . This feature opens the opportunity of choosing other air separation processes, besides cryogenic distillation, which provides only pure oxygen, at high costs, with advantages over that former one, such as lower capital investment (and therefore, low retrofit cost) and O&M costs, and less scale restrictions. In this way, technologies such as membrane separation are promising (Baukal, 1998).

Based on these assumptions, the present work assessed a combustion system coupled to an oxygen separation system source, allowing it to operate as an OEC system. In order to evaluate the inherent advantages and disadvantages of OEC technology, this system consists only by essential devices for implementing the enrichment of combustion. A mass and energy balance analysis was performed, observing some sustainability metrics, as energetic and exergetic efficiencies, fuel consumption and pollutant emissions. The membrane separation was chosen to be one of the most promising technologies for producing oxygen enriched streams for use in OEC processes. At the end, the separation process by polymeric membranes was confronted to cryogenics distillation process, which is the most usual method of air separation.

2. OEC BACKGROUND

Oxygen-enhanced combustion including oxygen separation from air by polymeric membranes has already been studied, but mostly experimentally, and for specific applications. As a consequence, these studies do not consider regeneration of waste streams, which have energetic and exergetic potential, such as the nitrogen-enriched flow resulting from membrane separation or the combustion exhaust gases, lacking, therefore, of a more detailed thermodynamic analysis.

Kimura and Browall (1986) studied natural gas combustion with oxygen-enriched fuel from a membrane. They showed that membrane is a potentially attractive process but requires a more detailed cost study, able to find the trade-

off between capital and operating costs. A silicone-based membrane was studied experimentally and results showed a reduction in natural gas consumption, due to the enrichment.

Rigby and Watson (1994) worked with enriched combustion for diesel engines, showing a significant reduction of particulate emissions (up to 80%) and an increased thermal efficiency under certain conditions. The experiment used a prototype flat sheet polymeric membrane module and was the first to identify a possible role for polymeric membrane applied to diesel engines.

Poola *et al.* (2000), studied through a thermodynamic analysis the effects of oxygen enriched oxidant on the performance and nitrogen (NO) emissions of a locomotive diesel engine. The results show that for a 4% increase in peak cylinder pressure can result in an increase in net power of approximately 13% when intake air with an oxygen content of 28% by volume is used. Furthermore, reduced levels of particulate can be obtained but NO emissions increase up to three times to 26% of O_2 in oxidizer.

Coombe and Nieh (2007) studied experimentally a polymeric membrane separation for combustion in portable liquid fuel burners. They showed that the required power for the membrane to operate is relatively low and can be justified against the benefices of OEC.

Qiu and Hayden (2009) observed the effect of oxygen-enrichment on radiant burners and used a polymeric membrane for oxygen separation. They showed that enrichment of 28% O_2 could lead to 22 to 28% potential natural gas savings.

3. OEC CYCLE SIMULATED

The present study analyses the behavior of a conventional combustion system, based on a natural gas fueled furnace, adapted to operate under OEC with a membrane based enrichment system, as depicted on Fig. 1:



Figure 1. Schematics for OEC system with oxygen enrichment unit

The system is fed with air at atmospheric conditions which is then compressed up to the required membrane operating pressure. A cooler issued to bring stream 1 back to environmental temperature before it is concentrated through the membrane. The high-pressure N_2 -enriched air stream, corresponding to the membrane retentate, is expanded in a recovery turbine (points 4 on Fig. 1). The enriched oxidant is then mixed to natural gas, right before the combustion chamber (point 7). Heat rejection before air separation and work recovery on the turbine placed after the pressurized output of the separation devices were specified so that their respective exit streams were in a common thermodynamic state, allowing for a base comparison of the system performances.

Oxygen enrichment was modeled by mass and energy balances, and combustion was solved using the chemical equilibrium hypothesis (flue gas formed by molecules of CO, NO, NO₂, H₂, OH, O, N, H₂O, CO₂, N₂ and H), which is a good approximation for gases produced in the combustion of gaseous fuels (Rashidi, 1997). All fluids were considered as ideal gases.

The molar flow rate of any species *i* that crosses the membrane is given by:

$$\dot{n}_i = A \left(\frac{P_i}{L}\right) \Delta p_{p,i} \tag{1}$$

where A is the membrane surface area (m²), P_i the membrane permeability (kmol µm kPa⁻¹ m⁻² s⁻¹), L the membrane thickness (µm) and $\Delta p_{p,i}$ the partial pressure difference between the permeate and retentate streams, for a given species *i* (Tessendorf, Gani and Michelsen 1999). Membrane selectivity and permeability are calculated for an optimal membrane, which corresponds to a membrane on the upper bound defined by Robeson (2008), as shown Fig. 2:



Figure 2. Upper bound correlation for O_2/N_2 separation (Robeson 2008).

Exergy (kW) was calculated for every point j of both systems, and the specific standard molar chemical exergy (kJ kmol-1) was taken according to Model II of chemical exergy values in the environment (Bejan, Tsatsaronis and Moran, Thermal design and optimization 1996). The destroyed exergy for a given component, limited by a control volume (kW) is given by:

$$\dot{E}x_{cv}^{d} = \sum \left(1 - \frac{T_{0}}{T}\right)\dot{Q}_{cv} - \dot{W}_{cv} + \sum \dot{n}_{in}ex_{in} - \sum \dot{n}_{out}ex_{out}$$
(2)

The exergetic efficiencies for each component were calculated by the ratio of exergetic products and fuel (Bejan, Tsatsaronis and Moran, Thermal design and optimization 1996). Thus, the overall energetic and exergetic efficiencies were defined respectively as:

$$\eta = \frac{\dot{Q}_{comb} + \dot{W}_t}{\dot{n}_6 + LHV + \dot{W}_t} \tag{3}$$

$$\varepsilon = \frac{\dot{E}x_{comb}^q + \dot{W}_t}{\dot{E}x_0 + \dot{E}x_6 + \dot{W}_c} \tag{4}$$

The specific emission e_i (kg/kJ) of a given specie *i* is expressed as the ratio of mass flow rate at point 8 to the summation of delivered heat and power by the system to the environment:

$$e_i = \frac{\dot{m}_{i,8}}{\dot{W}_i + \dot{Q}_{comb}} \tag{5}$$

computed for CO_2 , CO and NO. A total system emission in respect solely to CO_2 is calculated after Eq. (6), which includes the pollutants previously emitted for air compression via electrical power.

$$e_{CO_{2},tot} = \frac{\dot{m}_{CO_{2},8} + W_{c}e_{CO_{2}}^{el}}{\dot{W}_{t} + \dot{Q}_{comb}}$$
(6)

That last quantity $(e^{e_{CO2}})$ was particularized for the Brazilian electrical matrix, considered to be 82.1gCO₂/KWh (ABB 2012), in average.

4. RESULTS

4.1 Conventional combustion

The simulation routine was built with the aid of the EES software (Engineering Equation Solver, www.fchart.com), which is a general algebraic equation-solving program which integrates thermodynamic property libraries.

The performance assessment of the OEC option with oxygen separation by membrane was established against a reference case, where combustion is performed on the proposed system of Figure 4 without oxygen enhancement. The auxiliary devices (compressor, oxygen enrichment unit and expansion turbine) were simulated with zero flows and charge, simulating a regular atmospheric combustion situation. A fixed molar flow rate of CH₄ of 0.0005 kmol/s was defined for a stoichiometric combustion. Flue gas temperature at the output of the combustion chamber was also fixed ($T_8 = 1900$ K), considering that the effect of enrichment is higher when operating with high temperatures (Baukal, Oxygen-enhanced combustion 1998). Reference case main results are the heat exchange of 88.8 kW and and specific emissions of the three major pollutants: $e_{CO2} = 2.43 \times 10^{-4}$ kg/kJ, $e_{CO} = 2.77 \times 10^{-6}$ kg/kJ and $e_{NO} = 6.46 \times 10^{-7}$ kg/kJ.

4.2 Results for OEC combustion

Membranes with various permeabilities were considered, selectivity varying from 3 to 10, in accordance to Robeson (2008) recommendation on the available range of polymeric membranes.

In Eq. (1), once the selectivity is fixed and the molar flow rate defined, by stoichiometric conditions, there remains only two variables, membrane area and partial pressure difference (this one being directly related to the compression power). So, for a given selectivity and level of enrichment, the area was specified so that the compression power was minimal and this point was defined as the operating point under these conditions.

For each selectivity and level of enrichment, the membrane area, Eq. (1), was set as the area for which the compression power was minimal. This compression power and the associated area were then defined as the membrane operating point for the given selectivity and enrichment.

Figure 3 and Fig. 4 show the compressor power and the areas for various membrane selectivities.



Figure 3. Compressor power as a function of enrichment level for membranes with various selectivities and variable surface area (according to Fig. 4).



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Figure 4. Optimun membrane area as a function of enrichment level.

The compressor power evolution with enrichment shows that for each selectivity, there is a enrichment limit, after which the compressor power increases exponentially. This limit rises up to 50-55% for high selectivity membrane.

The required area increases with selectivity because, according to the figure from Robeson (2008), permeability decreases with selectivity. Besides, the area decreases with enrichment for a given selectivity. This is due to the fact that the permeate mass flow rate decreases (nitrogen is being removed from the oxidant) and the fact that the mass flow rate per unit area and compression ratio have been determined to minimize the compressor power.

The total energetic efficiency is shown on Fig. 5. The higher the membrane selectivity is, the higher the maximum efficiency. Compared with combustion with air, the increase in efficiency achievable is significant, ranging from 22% to 58%, and significant also for low levels of enrichment.



Figure 5. System efficiency for various selectivities as a function of enrichment.

The specific emissions were calculated by Eq. (5) and Eq. (6) and plotted on the next three figures as a relative specific emission, compared to the specific emission of the species for atmospheric combustion, i.e., the reference case data.



Figure 6. Relative specific CO₂ emissions eCO₂ and total relative specific CO₂ emissions e_{CO₂, tot}, for a membrane of selectivity 8 as a function of oxygen enrichment.



Figure 7. Relative specific CO emissions for a membrane of selectivity 8 as a function of enrichment



Figure 8. Relative specific NO emissions for a membrane of selectivity 8 as a function of enrichment.

Results on figures 6 to 8 show that the relative specific emissions for CO2, CO and NO for a membrane of selectivity 8, one of the best membranes currently available (Burdyny and Struchtrup 2010), decreases for the entire range of OEC operation, even for low levels of enrichment. For instance, an enrichment of 40% allows for emissions reductions of 60%.

It was verified that specific emissions and efficiencies remained practically unchanged when changing the fuel flow rate, considering a proportional membrane area. That same behavior was later noticed when running the system without OEC.

A comparative exergetic analysis was made, considering 3 different cases: combustion with atmospheric air and with 37% and 56% enriched air produced by a membrane of selectivity 8. That last one corresponds to the system maximum efficiency.

It can be seen in Fig. 9 that the destroyed exergy in the membrane increases with oxidant enrichment. In the combustion chamber, the destroyed exergy decreases with enrichment because of the lower chemical exergy destruction:



Figure 9. Destroyed exergy of the various components for different modes of operation.

Enrichment also allows for an increase of the transferred exergy in the combustion chamber, which is highest for a 56% enrichment. In the membrane case, the exergy loss in the cooler is higher with enrichment, because of the increase in compression power (Fig. 10):



Figure 10. Exergy transfer by heat in the various components for different modes of operation

The membrane efficiency also increases because the higher level of separation permits a proportional increase of the exit streams availability. With enrichment, the exergetic efficiency of the combustion chamber is increased. This is a direct consequence of the increase in available heat in the combustion chamber. The total exergetic efficiency of the membrane thermodynamic system increases with enrichment and would be even higher if all the exit streams would be used (for instance, the exit stream at 1900K could be used for another process, and that would increase this system total exergetic efficiency), as shown in Fig. 11 for main components:



Figure 11. Exergetic efficiency of main components for different modes of operation.

Currently, the oxygen production by cryogenics requires between 250 and 450 kWh/ton of O2 produced (Kauranen 2008). The result is that, it needs between 100 and 180 kWh to produce 1MWh of heat with cryogenics (considering the combustion of 1 ton of oxygen in this present model conditions). For a membrane of selectivity 8, the energy consumption for an enrichment of 37% corresponds to the maximum energy requirement by cryogenics (180kWh/MWh), that is why this point was represented on Fig. 12:



Figure 12. Energy consumption for the production of 1MWh of heat as a function of the production per day, for various techniques of oxidant production: cryogenics and membrane of selectivity 8. Data for cryogenics came from (Kauranen 2008).

Results suggest that membrane separation could be more interesting than cryogenics for smaller power plants. The size limit depends on the level of enrichment, because the compressor work rises very quickly with enrichment. For an enrichment of 37% for instance, the production limit is 200MWh/day.

5. CONCLUSIONS

This work has been a proof of concept with a particular oxygen enrichment system applied to oxygen-enhanced combustion, assessed by a thermodynamic simulation model. Operating curves were found for a polymeric membrane as a function of its selectivity, showing that a high selectivity allows for a higher level of separation and so a higher efficiency of the whole combustion system. This is promising as ongoing research on polymeric membranes tends to increase always more their selectivity. However, it has to be mentioned that the area required could be a limiting factor, as the selectivity increase makes permeability decrease, thus increasing the area required.

The exergetic analysis showed an improvement with enrichment as the destroyed exergy in the combustion chamber was reduced and the exergy transfer by heat increased. The simulated process showed to be energetically interesting if compared to cryogenics, for small scale production.

An economic analysis should be performed, comparing the membrane solution to cryogenics.

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