Thermodynamic study of oxygen-enhanced combustion: analysis of different techniques of oxidant production

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Abstract

Thermal energy is an important resource for many industrial processes and is usually produced by combustion of hydrocarbon fuels with air. These processes could benefit from the use of oxygen-enhanced combustion (OEC), whose benefits (pollutants emissions reduction, fuel savings, productivity increase and volumes reduction) are already known. However, low-cost oxygen production is still a challenge as the currently most used technique, cryogenics, is very energy consuming and costly. So, the present work proposes the thermodynamic analysis of two different techniques for production of oxidant required for the OEC process, the first one including air separation by polymeric membrane and the second one by PSA. Both systems were simulated on the software EES. Results show an increase of the energetic efficiency in both of the systems (from 22% to 58% in the membrane case and 66% in the PSA case) and of the exergetic efficiencies (from 18% to 48.5% and 54% respectively). A reduction of more than 60% of specific pollutants emissions was shown. The assessed techniques were shown to be energetically more attractive than cryogenics for small plants, the size limit depending on operating conditions.
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1 Introduction

1.1 Motivation
Heat for industrial processes is usually generated from combustion with air of hydrocarbon fuels as natural gas or oil. However, the Oxygen-Enhanced Combustion (OEC), which consists in combustion with an oxygen-enriched oxidant, can bring a series of advantages compared with conventional combustion. These improvements can be 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).

However, one of the major costs of operating an oxygen-enhanced combustion system lies in oxygen generation. OEC could be economically viable only if oxygen generation can be done at lower cost than with cryogenic distillation, which is currently the most used method. In this way, technologies such as membrane separation and/or pressure swing adsorption are promising (Baukal 1998).

Besides, natural gas being a type of fuel with lower emissions than coal and petroleum products, there is a global trend towards increased consumption of natural gas in the near future (EIA 2012). In the case of Brazil, natural gas is a fuel of major interest as the number of proved reserves on land with natural gas potential has increased drastically (see Annex I). According to the Brazilian National Petroleum Agency (ANP), that could lead to an increase in natural gas consumption of more than two-fold by 2020, going from 86 million cubic meters presently to 200 million (Mercopress 2012). Furthermore, in Brazil, natural gas and biomass are the two largest sources of thermal generation and power generation from natural gas more than doubled in 2010 (EIA 2012).

For these reasons and given the importance of integrating oxygen generation into the system, the present work proposes to study an OEC process coupled with oxygen generation, first by polymeric membrane separation and second by pressure swing adsorption, in order to evaluate the viability and benefits of those processes.

1.2 Literature review
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 revalorization of “waste” flows such as the nitrogen-enriched flow resulting from membrane separation or the exhaust gases.

In 1986, Kimura et al. studied natural gas combustion with oxygen-enriched fuel from a membrane. They showed that membrane is a potentially attractive process but requires a costs study and a trade-off must be found between capital costs and operating costs. A silicone-based membrane was studied experimentally and results showed a reduction in natural gas consumption, due to enrichment (Kimura and Browall 1986).

In 1994, Rigby et al. studied enriched combustion in diesel engines. They showed 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 in the area of diesel engines (Rigby and Watson 1994).

In 2007, Coombe et al. studied experimentally a polymeric membrane separation for combustion in portable liquid fuel burners. They showed that the power required for the membrane to operate is relatively low and can be justified in front of the benefits of oxygen-enhanced combustion (Coombe and Nieh 2007).
In 2009, Qiu et al. studied 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 (Qiu and Hayden 2009).

Although pressure swing adsorption (PSA) has already been presented as an option for oxygen separation for OEC (Baukal 1998), this application has not been studied yet. However, PSA has been widely studied for application to separation of various gases mixtures, including $O_2/N_2$ (Cruz, et al. 2003).

Two models are mainly used. The first one is the equilibrium model (Knaebel and Hill 1985) for which analytical solutions have been proposed (Banerjee, Narayankhedkar and Sukhatme 1989), (Chiang 1996). The second one is the linear driving force model (LDF) which takes into account a more accurate description of the adsorption effect (Cruz, et al. 2003) (Mendes, Costa and Rodrigues 2001).

Some authors proposed models between the analytical solution and a numerical simulation. Jain et al. proposed an heuristic model of PSA to provide easy rules for design of PSA and dimensioning of the most important parameters: adsorbent selection, particle and bed size, purge volume (Jain, et al. 2003). Serberzov et al. proposed a semi-analytical model, which allows finding some of the parameters analytically and only a range of possibility for the others (Serberzov and Sotirchos 2003).

### 1.3 Scope and objectives

The present work is based on a previous work about oxygen-enhanced combustion applied to gas turbine (Maidana, Carotenuto and Schneider, Analysis of oxygen-enhanced combustion of gas power cycle 2010). In the previous work was developed an EES (Engineering Equation Solver) code to model a gas turbine cycle. Pure oxygen was injected at high pressure in the compressed air feed before the combustion chamber, thus creating an oxygen-enriched oxidant. It was shown that using OEC could increase the system energetic efficiency or reduce the pollutants emissions, and bring many other advantages that depend on the application (see section 2).

This work intends to study OEC coupled with oxygen generation as a thermodynamic system. The respective processes were simulated with a code developed in EES, as did Maidana et al., that made a first analysis on EES of membrane separation applied to OEC, comparing three different types of membranes and performing an energetic analysis of the system (Maidana and Schneider, Energetic analysis of oxygen-enhanced combustion with air separation by polymeric membranes 2012).

The major difference of this work with previous studies is that the analysis will focus on the whole system including oxygen production and all the outlet flows, and that an exergetic analysis will be performed.

First, the OEC system was implemented and the model validated according to available data. Then, membrane separation was modeled and process simulations were realized. A PSA system was also modeled. Next, the two systems (separation system and combustion system) were coupled and the simulation results compared to conventional system. The feasibility and viability of the process was analyzed. Analysis of energetic efficiency, fuel consumption, pollutant emissions and exergetics were made in order to assess the sustainability of such a system. The systems were then compared to cryogenics.
2 Oxygen-enhanced combustion

2.1 Principle

2.1.1 Enrichment levels

Oxygen-enhanced combustion consists basically in increasing the oxygen concentration in the atmospheric air in order to create an oxidant enriched in oxygen, which is the species of interest for combustion applications. Atmospheric air can be approximated as composed of 21% of oxygen and 79% of nitrogen, in volume. In principle, OEC can be applied to any thermal process that implies burning of fuel. However, in a report for the Gas Research Institute, several applications were pointed out that could potentially benefit from OEC. They are processes with high flue gas temperatures, processes of low thermal efficiency, processes that have high level of emissions (especially NOx) or flue gas volume limitations (Baukal 1998).

The major difference of traditional combustion and OEC resides in the adiabatic flame temperature after combustion. Increasing O2 level leads to a substantially higher temperature (up to 3000 K).

The O2 mole fraction in the oxidant is defined as:

\[
\Omega = \frac{\text{volume flow rate of O2 in the oxidizer}}{\text{total volume flow rate of oxidizer}}
\]  \hspace{1cm} (2.1)

Three levels of enrichment are defined (Baukal 1998):

- Low-level enrichment (\(\Omega < 0.30\)): this is normally used for retrofit applications. In this case, only a few changes to an existing application need to be made in order to operate in OEC and bring various improvements to the process.

- Medium-level enrichment (0.30 < \(\Omega < 0.90\)): the interest of this type of combustion has grown only recently, and this operating mode requires specially designed burners. Membrane levels of enrichment are included in this region (see section 3.2).

- High-level enrichment (\(\Omega > 0.90\)): it is currently used when the need for high temperature or high purity of oxygen justifies the added cost of producing high purity oxygen, which is presently produced by cryogenics (see section 3.1). PSA would be integrated into this category, but would be justified only if lower costs are achievable.

2.1.2 Combustion reaction

The stoichiometric reaction of methane with air is represented by the following equation:

\[
CH_4 + 2(O_2 + 3.76 \ N_2) \rightarrow CO_2 + 2H_2O + 7.52N_2 (+ \text{ trace species})
\]  \hspace{1cm} (2.2)

In the case of oxygen-enhanced combustion, the stoichiometric reaction becomes:

\[
CH_4 + 2\left(O_2 + \frac{1-x_{O_2}}{x_{O_2}}N_2\right) \rightarrow CO_2 + 2H_2O + 2 \frac{1-x_{O_2}}{x_{O_2}}N_2 (+ \text{ trace species})
\]  \hspace{1cm} (2.3)

Where \(x_{O_2}\) is the molar fraction of O2 in the oxidant. By increasing the enrichment of oxidant, the nitrogen is in fact removed from the oxidant.

The equivalence coefficient for oxygen-enhanced combustion is defined as:
Combustion will be rich in oxidant if $\Phi < 1$ and rich in fuel if $\Phi > 1$.

The oxygen enrichment of the oxidant has as an effect the reduction of nitrogen volume in the oxidant and then in the flue gases. The quantities of the other flue gases compounds are dependent on the oxygen enrichment level $\Omega$, the exhaust gases temperature and the equivalence coefficient $\Phi$, which represents the actual ratio oxidant/fuel compared to the stoichiometry. If adiabatic equilibrium is considered, when solving for the flue gases composition, the major species obtained are CO, CO$_2$, H$_2$O and N$_2$. Proportions of these compounds in flue gases are shown on Figure 1.

![Figure 1 Major species concentrations vs oxidizer composition, for an adiabatic equilibrium stoichiometric CH$_4$ flame (Baukal 1998)](image)

### 2.2 Advantages and drawbacks

#### 2.2.1 Advantages

Baukal gives a series of advantages and drawbacks of OEC that are briefly summarized in this section (Baukal 1998).

The flame temperature increases significantly when oxygen concentration rises, because nitrogen is a diluent and reduces flame temperature. The peak flame temperature occurs at stoichiometric conditions ($\Phi=1$). So, the first possible advantage of OEC is the increased productivity. Indeed, in high temperature processes, heat transfer by radiation dominates. As radiation is dependent on the fourth power of absolute temperature, the increase of flame temperature associated with OEC leads to much higher radiation. This leads to the possibility of using much smaller systems if the space is important or increase productivity of an already existing system. Besides, the cost of changing the existing system to OEC is rather small compared to changing the whole system. So, the OEC system can be rather cheap to install as it can be done by modifying only a little an existing system and leads to improve rates of production.
OEC also leads to higher thermal efficiencies. Indeed, available heat increases when increasing oxygen concentration, because there is less nitrogen. Thus, the increase in efficiency is very significant when using an oxygen-enriched air. As a consequence, for a same amount of heat retrieved from combustion, less fuel is required. Some systems already achieved fuel savings of up to 60%.

Flame characteristics are improved with OEC. Indeed, the upper flammability limits almost increases linearly with the O₂ concentration, whereas the lower one remains more or less constant. So, the flammability range is broader, thus enabling the flame to exist under a wider range of conditions (this includes a wider range of Θ).

Another possible advantage is in the volume of exhaust gases, that also induces reduction of particulate emissions due to lower gas velocities at the system outlet. The reduction in the system size also inherently induces lower construction costs and less space requirement.

Besides, OEC can have many different advantages that are specific to the process which is being considered. For instance, in the glass industry, using higher temperatures allows for the product quality to be improved.

### 2.2.2 Drawbacks

However, OEC can also present some drawbacks: there is the risk for overheating as temperatures are generally higher and material should be adapted to these temperatures. Due to higher temperature gradients, hot spots are more easily created and should be avoided. Besides, corrosive particulates can create problems with the materials.

Furthermore, as a consequence of exhaust gases volume reduction, the convective heat transfer to the load from exhaust gases can be reduced. NOₓ emissions can become higher as the temperature increases thus enabling the production of more thermal NOₓ (produced at high temperatures from N₂ in feed air).

There is also a potential risk of flashback. Indeed, as the flame velocity increases, the velocity of gases should be higher in order to prevent flashbacks.
3 Oxygen production

3.1 Cryogenic processes

Presently, cryogenic air separation is the most efficient technology to produce large quantities of oxygen at lowest costs (Smith and Klosek 2001). It can produce amounts of oxygen up to 3000t/day with purity between 90 and 99.9% (Baukal 1998).

The technology consists of five major unit operations. First, an air pretreatment section removes process contaminants: water, carbon dioxide and hydrocarbons. Then, the air is cooled to cryogenic temperatures and distilled into oxygen and nitrogen (sometimes argon is also separated). The products are then warmed against the incoming feed and compressed before delivery. Many configurations of the system are possible, depending on required purity and product streams (Smith and Klosek 2001). Figure 2 illustrates a general cryogenic process.

According to Kauranen, oxygen production by cryogenics requires between 250 and 450 kWh/ton of O₂ produced (Kauranen 2008). This energy consumption decreases with the production volumes. This curve is represented on Figure 41.

3.2 Membranes

3.2.1 Definition

Membranes are thin barriers that are semipermeable to some compounds and that selectively allow one or some compounds more than others. There is a wide variety of membrane materials, and the material choice depends on the operating conditions and the purpose of the system (Dortmundt and Doshi 1999).

3.2.2 Membranes for air separation

For oxygen separation from air, preference is given to polymeric membranes and from a few years also to ceramic-based membranes.

The diffusion of some gas compounds through polymeric membranes is driven by pressure difference between the two sides of the membrane. As the oxygen molecule has a smaller size than that of nitrogen, membranes are usually more permeable to oxygen. Membrane systems do not give pure oxygen as a product but an oxygen-enriched air. The oxygen-enriched stream oxygen concentration usually ranges from 25% to 50% in volume and polymeric membrane systems can provide up to 20 tons/day of enriched stream (Smith and Klosek 2001). They operate at ambient temperatures (Hashim, Mohamed e Bhatia 2010).

More recently emerged another category of membranes which are called ceramic membranes and operate at higher temperatures (800 to 900ºC) (Hashim, Mohamed e Bhatia 2010). However, the purpose in this
study is to focus on polymeric membranes as they are more widely studied and already used in industrial processes (Dortmundt and Doshi 1999).

3.2.3 Membrane choice

Two parameters that indicate the behavior of a membrane and that are thus important when selecting a membrane are permeability (P) and selectivity (α). Permeability is related to the quantity of gas that can pass through the membrane. As a consequence, for a given required mass flow of one gas compound through the membrane, the higher the permeability will be, the lower the membrane area requirement. Membrane area requirement has a cost, and tendency is to try to lower it. Permeability is commonly given in Barrers (1 Barrer = 0.33 x 10^{-15} mol m/m² s Pa).

Membrane selectivity represents how much the membrane will let go through one compound over another. In the process of oxygen separation from air, the membrane selectivity of O₂ over N₂ is defined by:

\[ \alpha = \frac{P_{O_2}}{P_{N_2}} \]  

(3.1)

It has been recognized that selectivity decreases when the permeability of the most permeable component increases. As a consequence, one needs to find a trade-off between those two parameters when selecting the membrane. In his article, Robeson showed the existence of an upper limit of selectivity as a function of permeability for currently available membranes (Robeson 2008). Figure 3 shows permeability and selectivity of currently available membranes (red circles) and draws the upper limit for O₂/N₂ separation.

![Figure 3 Upper bound correlation for O₂/N₂ separation (Robeson 2008)](image)

If the system consists of a single membrane, the principle of operation is simple. A pressure difference is created between the two sides of the membrane. Either the air is compressed at the entrance or vacuum is created at the exit. The mass flow rates of the different compounds of air are then controlled by permeability and area. Two streams are collected: the permeate stream, oxygen enriched, and the retentate stream, nitrogen enriched (Figure 4).
3.2.4 Membrane elements

There are two existing forms of membranes: flat sheets and hollow fiber. Flat sheets are combined in order to form a spiral-wound element (Figure 5), and hollow fibers are assembled into a bundle (Figure 6). Each of these techniques has their advantages. Spiral-wound elements can work at higher pressure and are already widely used for natural gas sweetening. However, hollow fiber membranes have a higher density and require less space for their installation (Dortmundt and Doshi 1999). Membrane elements are then joined together in order to form the complete structure.

3.2.5 Advantages and drawbacks

Membrane systems have various advantages over the commonly used cryogenic distillation. First, membrane separation is a simple and continuous process and usually operates at conditions closed to ambient conditions (in the case of polymeric membranes), making it an attractive option (Smith and Klosek 2001). Besides, the process is relatively passive and only requires work of compression, which makes it less costly to operate. Polymeric membranes are already widely studied and a lot of data is available about them. Ceramic membranes however are still at a research state and much remains to be done.
However, membrane requires high initial investments compared to existing processes (Robeson 2008) and can only produce oxygen-enriched air and not pure oxygen. They also produce at lower flow rates than cryogenic separation, but with ongoing research, membrane processes will improve in cost and energy efficiency and could challenge cryogenic technology for smaller flow rates and when lower enrichment levels are required.

### 3.3 Pressure/Vacuum swing adsorption (PSA/VSA)

#### 3.3.1 Operation principle

PSA and VSA processes are based on adsorption of one or more components of a gas mixture on a bed. Some synthetic or natural materials preferentially adsorb nitrogen. This is the case of zeolites for instance, where non-uniform electric fields cause nitrogen to be preferentially adsorbed, and when a mixture of oxygen/nitrogen goes through a zeolite bed, an oxygen-enriched stream is created at the outlet. Zeolites are a typical material used for oxygen separation by adsorption (Smith and Klosek 2001).

After being saturated with nitrogen, the bed is regenerated using total or partial pressure decrease. The difference between PSA and VSA is only the range of pressures that are used. PSA usually works between the ambient pressure and a higher one and VSA between ambient pressure and a lower one (vacuum). They have been used as a cheap and efficient alternative to conventional processes of separation of gases. The first PSA system used for the separation of oxygen from air was implemented in 1964 (Cruz, et al. 2003).

The most basic PSA/VSA system uses the classical Skarstrom’s cycle in a two-bed configuration. This cycle is composed of four main steps: pressurization with feed, high-pressure production, depressurization and purge. This means that first, pressurized air enters one bed in order to increase the bed pressure to the highest pressure of operation. Nitrogen is then adsorbed until the bed becomes saturated, the feed air continuing to enter the column. Then, the feed air goes to a fresh vessel and the first bed enters into the regeneration step, which consists in bed depressurization. This makes the nitrogen adsorption capacity smaller and thus causes the nitrogen to leave the bed. Purge step then consists in using a part of the oxygen-enriched stream leaving the other bed to remove nitrogen from the first bed. Figure 7 shows the basic principle of operation of a PSA/VSA system.

![Figure 7 Scheme of a two fixed-bed PSA system (Cruz, et al. 2003)](image)
The different stages of the system operation and their names are presented on Table 1. The advantage of using a two-bed configuration is that while one bed is producing, the other one is regenerating, allowing for an almost continuous production in spite of PSA being a cyclic process. Generally, for oxygen production, only two beds are used because the air is free, it is more economically interesting to use only two columns (recovery of oxygen is not as important as recovery of a fuel that would be expensive to buy).

A pretreatment aiming at removing water and carbon dioxide from the incoming air is commonly used before entering the columns. Many parameters affect the system efficiency and system optimization should focus on the product flow, purity and pressure as well as energy cost and operating life. PSA/VSA systems allow producing a stream with 93-95% oxygen in volume. The major factor that affects initial costs is the bed size, which is a major factor because it controls the product flow rate (Smith and Klosek 2001).

One important parameter to assess PSA performance is recovery. By definition, recovery is the quantity of oxygen retrieved in the high-pressure product divided by the quantity of oxygen in the feed air.

After the high-pressure production step in one column (purge step in the other), a pressure-equalization step can be added. This step consists in connecting the two beds by their product end and make the pressure equalize between them. This is a very important step that is used in most of industrial processes (Banerjee, Narayankhedkar and Sukhatme 1989) because significant quantity of energy is saved as less mechanical energy is required to pressurize the column. Besides, recovery is also increased as no less feed air is required to pressurize the column (Cruz, et al. 2003).

### 3.3.2 Analytical solution of equilibrium model

An analytical solution of an equilibrium model was developed by Knaebel et al. (Knaebel and Hill 1985) and completed by Banerjee et al. (Banerjee, Narayankhedkar and Sukhatme 1989). The assumption of equilibrium means that product is pure oxygen, which is only an approximation of real cases.

In their solution, the system was a two-column PSA process with identical beds. The process included the four usual steps of the classical Skarstrom cycle and an additional pressure equalization step. In the system, pressurization was be made by product, given that it has been proven to be superior to pressurization by feed (Knaebel and Hill 1985).

The assumptions that were made to solve the system equations were:

- Isothermal behavior of the system at operating pressures.
- Dissipative effects are neglected.
Most important equations are described in this section, and for more detailed resolution, see Annex II. A mass balance equation in one column can be written, for the total mass and for nitrogen respectively:

\[
\frac{\partial P}{\partial t} + \frac{\partial (Pv)}{\partial z} + \frac{RT(1 - \epsilon^*)}{\epsilon^*} \frac{\partial n}{\partial t} = 0
\]  \(3.2\)

\[
\frac{\partial p_{p,N_2}}{\partial t} + \frac{\partial (p_{p,N_2}v)}{\partial z} + \frac{RT(1 - \epsilon^*)}{\epsilon^*} \frac{\partial n_{N_2}}{\partial t} = 0
\]  \(3.3\)

To assess the number of moles absorbed per unit volume \(n\), equilibrium isotherm are used. The simplest model is the Henry’s law which states that:

\[n_i = k_i C_i\]  \(3.4\)

\(C_i\) being the molar concentration of species \(i\) in the fluid phase and \(k_i\) the Henry’s law coefficient. This concentration can be written (using the ideal gas law):

\[C_i = \frac{p_{p,i}}{RT}\]  \(3.5\)

As a result:

\[n = n_{N_2} + n_{O_2} = \frac{(k_{N_2}p_{p,N_2} + k_{O_2}p_{p,O_2})}{RT}\]  \(3.6\)

Solving these equations for each step leads to the number of moles entering and leaving the columns in each step:

\[N_{PR} = \phi\beta L^*(\pi - \sqrt{\pi})\]  \(3.7\)

\[N_F = \phi L^*\pi\]  \(3.8\)

\[N_{PO} = \phi L^*\pi(1 + (\beta - 1)y_F)\]  \(3.9\)

\[N_{PU} = \phi L\]  \(3.10\)

The product recovery can then be defined as:

\[Rec = \frac{N_{PO} - N_{PR} - N_{PU}}{N_F(1 - y_F)}\]  \(3.11\)
4 Methodology

4.1 Thermodynamic cycles

Two thermodynamic cycles were defined, that consist in:

- A cycle including oxygen separation by polymeric membrane and oxygen-enhanced combustion.
- A cycle including oxygen separation by PSA and oxygen-enhanced combustion.

4.1.1 Cycle including membrane

A thermodynamic cycle including membrane separation and oxygen-enhanced combustion was created (Figure 8). The system created started with air at atmospheric conditions of pressure and temperature (dead state).

First, feed air goes through a compressor (state 0 to 1) in order to be compressed up to the membrane operating pressure. Compression induces a rise in air temperature. Usually, a vacuum pump is used with membranes, but as the objective of this study is to study the feasibility of the membrane process also for larger scales, a compressor was used in order not to limit the volumetric flow. After the compressor, air goes through a cooler (1 to 2), where its temperature is decreased to the polymeric membrane operating temperature. The air then goes through the membrane (2 to 3, 4), where it is separated in two streams: the permeate (2), enriched in oxygen and the retentate (4), poorer in oxygen. Retentate stream is then expanded through a turbine (4 to 5) and is brought back to atmospheric pressure. On the other side, permeate is premixed with fuel, which is natural gas (considered as composed exclusively of CH₄) and the mixed stream enters the combustion chamber, where combustion takes place at atmospheric pressure.

4.1.2 Cycle including PSA

A second thermodynamic cycle, including oxygen production by PSA and oxygen-enhanced combustion was created (Figure 9). As well as in the previous system, air enters at atmospheric conditions of pressure and temperature.

The air is then compressed in the compressor (point 0 to 1), and by doing so, its temperature is increased. As the PSA is operated at a temperature close to ambient temperature (T = 303K), a cooler is used to...
decrease the air temperature to ambient temperature. Then the oxygen is separated by a two-bed PSA system (2 to 3, 4). An oxygen storage tank is used as the PSA is not a continuous process. By using it, the system behaves as if the supply of oxygen-enriched stream to the rest of the system was constant. This oxygen-enriched stream is then expanded through a turbine until it reaches atmospheric pressure, as the oxygen is produced at high pressure (point 3 to 5). A mixer is then used to premix the oxidant and fuel (5, 6 to 7) and finally the combustion takes place in the combustion chamber (7 to 8).

![Figure 9 Thermodynamic system 2, including oxygen production by a two-bed PSA process](image)

### 4.2 Components modeling

The thermodynamic systems presented above were simulated using the software EES (Engineering Equation Solver), which is a general equation-solving program that integrates calculation of thermodynamic properties of various elements. In the simulations, all fluids were considered as ideal gases. This section presents the equations that were used to simulate the processes.

#### 4.2.1 Feed

The dead state is defined by:

\[
T_0 = 298.15 \; K \\
p_0 = 101.325 \; kPa
\]

#### 4.2.2 Compressor

The compressor is considered as ideal (isentropic efficiency is 1), since the objective is to assess the sustainability of OEC process. It is used to compress the air from the atmospheric pressure \( p_0 \) to the pressure of membrane (for system 1) or PSA (for system 2) operation.

Pressure at compressor outlet is \( p_1 = p_0 r_c \), where \( r_c \) is the compression ratio, which, for system 1, depends on membrane operation and for system 2, is defined (see section 4.2.5). Mass conservation equation is written: \( \dot{n}_1 = \dot{n}_0 \). Assuming that \( s_1 = s_0 \), and from the gas properties, enthalpies at the inlet and outlet are calculated and the compressor work is calculated by:
\[ W_c = \dot{n}_1 (\bar{h}_1 - \bar{h}_0) \] (4.1)

### 4.2.3 Cooler

Cooler is needed between the compressor and the membrane in order for the gas to be decreased to membrane/PSA operating temperature \( T_2 \). The cooler is simulated as an infinite heat exchanger. Pressure remains constant: \( p_2 = p_1 \). In the cooler, molar flow is conserved: \( \dot{n}_2 = \dot{n}_1 \) and the composition of gases remains the same. The heat delivered to atmosphere from the heat exchanger is:

\[ \dot{Q}_{\text{cooler}} = \dot{n}_2 (\bar{h}_2 - \bar{h}_1) \] (4.2)

The enthalpies are calculated from the gases properties at given temperatures.

### 4.2.4 Membrane

Only the two species nitrogen (79%) and oxygen (21%) were considered in the simulations. Table 2 shows the membrane operating parameters.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Feed</th>
<th>( p_2 = p_0 \times r_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Permeate</td>
<td>( p_3 = p_0 )</td>
</tr>
<tr>
<td></td>
<td>Retentate</td>
<td>( p_4 = p_2 )</td>
</tr>
<tr>
<td>Temperature</td>
<td>( T_3 = T_4 = T_2 )</td>
<td></td>
</tr>
</tbody>
</table>

The molar flow rate of any compound \( i \) that crosses the membrane is given by:

\[ \dot{n}_i = A \left( \frac{P_i}{L} \right) \Delta p_{p,i} \] (4.3)

In this equation, \( \dot{n}_i \) is the molar flow rate of compound \( i \), \( A \) is the membrane area, \( P_i \) the permeability of the membrane to component \( i \), \( L \) the membrane thickness and \( \Delta p_{p,i} \) the difference of partial pressure of component \( i \) on the two sides of the membrane.

It was considered that the partial pressure difference is taken from the permeate and retentate streams compositions (Tessendorf, Gani and Michelsen 1999). Using the notations as given on Figure 8, the equation for the molar flow rate becomes:

\[ \dot{n}_{i,3} = A \left( \frac{P_i}{L} \right) \left( x_{i,4} p_4 - x_{i,3} p_3 \right) \quad i = \{O_2, N_2\} \] (4.4)

The second equation which is necessary is the mass conservation for each species:

\[ \dot{n}_{i,2} = \dot{n}_{i,3} + \dot{n}_{i,4} \quad i = \{O_2, N_2\} \] (4.5)

Which in terms of total molar flow rates becomes:

\[ x_{i,2} \dot{n}_2 - x_{i,3} \dot{n}_3 - x_{i,4} \dot{n}_4 = 0 \quad i = \{O_2, N_2\} \] (4.6)

Equations of the composition of each stream are needed:

\[ x_{O_2,3} + x_{N_2,3} = 1 \] (4.7)
\[ x_{O_2,4} + x_{N_2,4} = 1 \] (4.8)

Finally, the energy equation is written:
Membrane selectivity and permeability are calculated for an optimal membrane which corresponds to a membrane on the upper bound defined by Robeson (Robeson 2008). From this graph (Figure 3), an equation for the present upper bound is found:

\[
P_{O_2} = 1.4689 \cdot 10^6 \alpha^{-169/30} \text{ Barrers}
\]

\[
P_{O_2} = 0.33 \cdot 1.4689 \cdot 10^{-3} \alpha^{-169/30} \text{ kmol. µm. kPa}^{-1} \text{ m}^{-2} \text{ s}^{-1}
\]

### 4.2.5 Pressure Swing Adsorption columns

The pressure swing adsorption columns were modeled using the analytical solution described in section 3.3.2. The modeled system is a two-column PSA process with identical beds of zeolite 5A, which is the most used material for oxygen separation (Sircar, Rao and Golden 1998).

Table 3 shows the PSA thermodynamic conditions. The PSA operates between a low pressure which is the atmospheric pressure and a high pressure which is equal to the pressure after the compressor.

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Feed</th>
<th>( p_2 = p_0 \times r_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>( p_3 = p_2 = P_H )</td>
<td></td>
</tr>
<tr>
<td>Retentate</td>
<td>( p_4 = p_0 = P_L )</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>( T_3 = T_4 = T_2 )</td>
<td></td>
</tr>
</tbody>
</table>

The equations that are necessary for the simulations are:

- Mass balance equation:
  \[
x_{i,2} \dot{n}_2 - x_{i,3} \dot{n}_3 - x_{i,A} \dot{n}_4 = 0 \quad i = \{O_2, N_2\}
\]

- Streams composition:
  \[
  \begin{cases}
    x_{O_2,3} = 1 \\
    x_{N_2,3} = 0 \\
    x_{O_2,A} + x_{N_2,A} = 1
  \end{cases}
\]

- Recovery calculation:
  \[
  Rec = \frac{N_{PQ} - N_{PR} - N_{PU}}{N_F(1 - y_F)}
\]

- Recovery definition:
  \[
  Rec = \frac{x_{O_2,3} \dot{n}_3}{x_{O_2,2} \dot{n}_2}
\]

- The energy equation which is exactly the same as for the membrane system (5.9).

The values of the different parameters were retrieved from data from the literature (see Appendix B).

### 4.2.6 Turbine

The turbine is considered as ideal, as well as the compressor (isentropic efficiency equal to 1, mechanical and electrical efficiencies are also 1). At the turbine inlet, temperature is equal to the temperature of isothermal operation of membrane or PSA: \( T_4 = T_2 \) and pressure is the pressure of compressed air from
air compressor: \( p_4 = p_0 \cdot r_c \). As for the compressor, enthalpies at the inlet and outlet are calculated assuming that \( \bar{s}_4 = \bar{s}_5 \) and that the turbine outlet pressure is the atmospheric pressure: \( p_5 = p_0 \).

The turbine work output is then given by:

\[
W_t = \dot{n}_4(\bar{h}_4 - \bar{h}_5)
\]  

(4.16)

The definitions for the PSA cycle are the same except that point 4 is replaced by point 3.

### 4.2.7 Mixer

The mixer is used to premix fuel (natural gas) and oxidant. Natural gas is considered to be composed of 100% methane for simplification of the analysis. The equations for this mixer are the mass balance equation which is, in the case of the membrane cycle:

\[
\dot{n}_7 = \dot{n}_6 + \dot{n}_3
\]

(4.17)

And the energy conservation:

\[
\dot{n}_7 \bar{h}_7 = \dot{n}_6 \bar{h}_6 + \dot{n}_3 \bar{h}_3
\]

(4.18)

For the PSA cycle, there is the same set of equations where the subscript 3 is replaced by 5.

### 4.2.8 Combustion chamber

In order to solve the equations of combustion, the model explained by Maidana et al. was used (Maidana, Carotenuto and Schneider, Analysis of oxygen-enhanced combustion of gas power cycle 2010). This model was developed as an EES code, assuming that all the species are in chemical equilibrium after combustion at the adiabatic flame temperature. It applies for the combustion of air and oxygen-enriched air with natural gas (considering that natural gas is only CH\(_4\)) and includes the production of NO, CO, CO\(_2\), which are the three major pollutants created from the combustion of air with natural gas and H\(_2\), OH, O and H that are created in smaller quantities (Maidana, Carotenuto and Schneider, Analysis of oxygen-enhanced combustion of gas power cycle 2010).

The model is based on the minimization of the Gibbs function of the system composed by the gaseous species in the combustion chamber. The most important chemical reactions that can occur within the combustion chamber are written, and for each reaction of the type \( v_1A + v_2B \rightleftharpoons v_3C + v_4D \) the equilibrium constant is defined as:

\[
K = \frac{x_C^{v_3}x_D^{v_4}}{x_A^{v_1}x_B^{v_2}} \left( \frac{p_D}{p_0} \right)^{v_4+v_3-v_2-v_1}
\]

(4.19)

This constant is related to the Gibbs energy variation \( \Delta G \) in the reaction by:

\[
K = e^{(-\Delta G/RT_B)}
\]

(4.20)

(Maidana, Carotenuto and Schneider, Analysis of oxygen-enhanced combustion of gas power cycle 2010)

As in the present case, the objective of the combustion chamber is to transfer heat to the load by convection and radiation, the temperature out of the combustion chamber is desirably lower than the adiabatic flame temperature (for which the heat transfer is zero) and this temperature determines the exhaust gases chemical composition. In the present study, the outlet temperature was fixed as: \( T_B = 1900K \).

And the pressure in the combustion chamber is the atmospheric pressure, \( p_B = 101,325 \text{ kPa} \).

These equations were implemented in EES, to determine the exhaust gases composition. To determine the heat transferred to the load, an energy balance equation is written:
\[ \dot{n}_T \tilde{h}_T = \dot{Q}_{comb} + \dot{n}_B \tilde{h}_B \]  

(4.21)

The combustion model was compared to data from the literature and was shown to be an accurate model (see Appendix A).

### 4.3 Indicators for results analysis

#### 4.3.1 Fuel savings

Fuel savings correspond to the percentage of fuel that is saved when producing the same quantity of heat, with enriched and atmospheric air. Fuel savings are defined as:

\[
F_{\text{savings}} = \left[ 1 - \frac{(\dot{Q}_{comb})_{\text{base case}}}{(\dot{Q}_{comb})_{\text{actual}}} \right] \times 100
\]  

(4.22)

#### 4.3.2 Energetic analysis

There are three main energy flows in the system:

- The compressor power \( \dot{W}_c \)
- The turbine power \( \dot{W}_t \)
- The heat transfer to the load in the combustion chamber \( \dot{Q}_{comb} \)

Our study focus mainly on these flows, so the system total efficiency was defined as:

\[
\eta_{tot} = \frac{\dot{Q}_{comb} + \dot{W}_t}{\dot{n}_b \times \text{LHV} + \dot{W}_c}
\]  

(4.23)

#### 4.3.3 Exergetic analysis

##### 4.3.3.1 Availability and exergy balance

The exergy, which is equal to the availability, at one point \( j \) of the system is composed of two parts: physical exergy and chemical exergy. The standard molar chemical exergy \( \bar{e}_i^0 \) was considered to be the one given by the Model II in the book from Bejan et al. (Bejan, Tsatsaronis and Moran 1996).

The destroyed exergy in one component (represented by the controle volume \( cv \)) is given by:

\[
\dot{E}_{\text{x}}^{d}_{cv} = \sum \left[ (1 - \frac{T_0}{T}) \dot{Q}_{cv} - \dot{W}_{cv} + \dot{n}_{in} \text{ex}_{in} - \dot{n}_{out} \text{ex}_{out} \right]
\]  

(4.24)

The term \( \sum \left(1 - \frac{T_0}{T} \right) \dot{Q}_{cv} \) represents the exergy transferred by heat. In the case of a heat exchanger for instance, this can represent the exergy which is transferred from one flow to the other. This term will be used later as:

\[
\dot{E}_{\text{x}}^{Q}_{cv} = \sum \left(1 - \frac{T_0}{T} \right) \dot{Q}_{cv}
\]  

(4.25)

##### 4.3.3.2 Exergetic efficiencies

For each component, an exergetic efficiency can be defined, depending on the utilization of this component (Bejan, Tsatsaronis and Moran 1996). Definitions are summarized in Table 4.
Table 4 Definition of the components exergetic efficiencies

<table>
<thead>
<tr>
<th>Component</th>
<th>Membrane system</th>
<th>PSA system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exergetic</td>
<td></td>
</tr>
<tr>
<td>Component</td>
<td>Position in the</td>
<td>Position in the</td>
</tr>
<tr>
<td></td>
<td>system</td>
<td>system</td>
</tr>
<tr>
<td>Compressor</td>
<td>$\dot{W}_c$</td>
<td>$\dot{W}_c$</td>
</tr>
<tr>
<td>$\dot{q}_{comb}$</td>
<td>$\dot{E}x_0 - \dot{E}x_0$</td>
<td>$\dot{E}x_0 - \dot{E}x_0$</td>
</tr>
<tr>
<td>Cooler</td>
<td>$\dot{E}x_{\text{cool}}$</td>
<td>$\dot{E}x_{\text{cool}}$</td>
</tr>
<tr>
<td>Membrane</td>
<td>$\dot{E}x_3 + \dot{E}x_4$</td>
<td>$\dot{E}x_3 + \dot{E}x_4$</td>
</tr>
<tr>
<td>Turbine</td>
<td>$\dot{W}_t$</td>
<td>$\dot{W}_t$</td>
</tr>
<tr>
<td>$\dot{E}x_5$</td>
<td>$\dot{E}x_5$</td>
<td>$\dot{E}x_5$</td>
</tr>
<tr>
<td>Mixer</td>
<td>$\dot{E}x_7$</td>
<td>$\dot{E}x_7$</td>
</tr>
<tr>
<td>Combustion chamber</td>
<td>$\dot{E}x_{\text{comb}}$</td>
<td>$\dot{E}x_{\text{comb}}$</td>
</tr>
</tbody>
</table>

The total exergetic efficiency is defined as:

- For the case of combustion with air:
  $$\varepsilon_{\text{tot}} = \frac{\dot{E}x_{\text{comb}}}{\dot{E}x_0 + \dot{E}x_6}$$  (4.26)

- For the case of OEC:
  $$\varepsilon_{\text{tot}} = \frac{\dot{E}x_{\text{comb}} + \dot{W}_t}{\dot{E}x_0 + \dot{E}x_6 + \dot{W}_c}$$  (4.27)

In this definition, only the three main energy flows, defined above, appear in the efficiency. The exergy transfer in the cooler and the exergy of the outlet stream from the combustion chamber were not taken into account (see section 5.4.3.2).

### 4.3.4 Emissions

The emissions associated to the system are calculated in grams per kilojoule of heat and electricity produced. Two types of emissions are defined: the emissions directly produced by the system, calculated for CO$_2$, CO and NO by equation (5.31); and the total emissions, calculated only for CO$_2$ by equation (5.32), which include the pollutants emitted previously when producing the electrical power required for compression.

$$\varepsilon_t = \frac{m_{\text{LB}}}{W_t + Q_{\text{comb}}}$$  (4.28)
The quantity of CO\(_2\) which is emitted for electricity production in Brazil will be considered to be in average: \(e_{\text{CO}_2}^\text{tot} = 82.1 \, \text{gCO}_2/\text{kWh}\) (ABB 2012).

### 4.4 Parameters and variables

The different parameters and variables that are used in the simulations are summarized in Table 5 and Table 6.

<table>
<thead>
<tr>
<th>Table 5 Simulations main parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Air compressor</strong></td>
</tr>
<tr>
<td>(T_0 = 298.15 , K , (25^\circ\text{C}), p_0 = 101.325 , kPa)</td>
</tr>
<tr>
<td>(x_{O_2,0} = 0.21, x_{N_2,0} = 0.79)</td>
</tr>
<tr>
<td>(T_3 = 298.15 , K , (25^\circ\text{C}), p_3 = 101.325 , kPa)</td>
</tr>
<tr>
<td>(T_4 = 298.15 , K , (25^\circ\text{C}))</td>
</tr>
<tr>
<td>(\beta_\alpha = 0.08569, \beta_\beta = 0.1454, \epsilon^* = 0.478)</td>
</tr>
<tr>
<td>(p_5 = 10.325 , kPa)</td>
</tr>
<tr>
<td>(\eta_\epsilon = 1)</td>
</tr>
<tr>
<td><strong>Membrane (for system 1 only)</strong></td>
</tr>
<tr>
<td>(T_3 = 298.15 , K , (25^\circ\text{C}), p_3 = 101.325 , kPa)</td>
</tr>
<tr>
<td>(T_4 = 298.15 , K , (25^\circ\text{C}))</td>
</tr>
<tr>
<td>(\beta_\alpha = 0.08569, \beta_\beta = 0.1454, \epsilon^* = 0.478)</td>
</tr>
<tr>
<td>(p_5 = 10.325 , kPa)</td>
</tr>
<tr>
<td>(\eta_\epsilon = 1)</td>
</tr>
<tr>
<td><strong>Mixer</strong></td>
</tr>
<tr>
<td>(p_7 = 101.325 , kPa)</td>
</tr>
<tr>
<td>(\phi = 1)</td>
</tr>
<tr>
<td></td>
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<tr>
<td>----------------</td>
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<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Membrane (for system 1 only)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Turbine</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Mixer</td>
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<tr>
<td></td>
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<td></td>
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</tbody>
</table>
5 Results and discussion

5.1 Base case

For the simulations, a base case is defined, based on a fixed molar flow rate of CH$_4$ (this value was taken from the previous work by Maidana et al.):

\[ \dot{n}_{CH_4} = 0.0005 \text{ kmol/s} \]

In this base case, combustion occurs without air enrichment. For the stoichiometric combustion of this quantity of natural gas in air, is required the quantity of air:

\[ \dot{n}_{air} = 0.004962 \text{ kmol/s} \]

In the stoichiometric case, the adiabatic flame temperature is 2223K. The temperature after the combustion chamber was fixed:

\[ T_b = 1900K \]

In this case, the heat exchanged in the combustion chamber is:

\[ \dot{Q}_{comb} = 88.84 \text{ kW} \]

Emissions of the three major pollutants, given on the basis of heat released during combustion $Q_{comb}$, are:

\[ e_{CO_2} = 2.433 \times 10^{-4} \text{ kg/kJ} \]
\[ e_{NO} = 6.461 \times 10^{-7} \text{ kg/kJ} \]
\[ e_{CO} = 2.766 \times 10^{-6} \text{ kg/kJ} \]

It was proven that, when making the fuel molar flow vary, the results are the same for the emissions and efficiencies and are proportional to the fuel flow rate for the area, compressor and turbine powers, heat from combustion.

5.2 Combustion under stoichiometric conditions and constant fuel feed

5.2.1 Energy flows, volume and fuel savings

The case studied considered combustion of natural gas with enriched air at stoichiometric conditions ($\Phi = 1$). The feed stream of fuel is maintained constant and equal to 0.0005 kmol/s (as in the base case). Under these conditions, the molar flow rate of the oxygen into the combustion chamber is constant, as required to ensure stoichiometry, but the total oxidant flow rate is reduced as the oxidant is enriched (enrichment in this case means removing nitrogen from the feed) (Figure 10).
For practical reasons, only the second subsystem (composed of 3, 6, 7, 8) is considered in this section, which allows concentrations of $\text{O}_2$ up to 100%. Then, the membrane/PSA will be coupled to this system. Results are presented as a function of the $\text{O}_2$ volume fraction in the oxidant.

As can be seen on Figure 11, heat transferred during the combustion is drastically increased by oxygen enrichment. This result also proves the validity of the combustion model as the same graph was found by Baukal (Baukal 1998). However, it can also be seen that the increase in available heat with enrichment is higher as the combustion chamber outlet temperature is higher. For outlet temperatures close to the ambient, enrichment does not bring advantages over combustion with air. However, in practical applications, exhaust gases temperature are high, and in this study, the results will be presented for an outlet temperature $T_8 = 1900$K. This temperature was proposed, as it was found to be studied in the literature (Baukal 1998), and is a temperature at which the advantages from OEC are significant.

Another advantage of OEC is the reduction of exhaust gases volume. This can be seen on Figure 12. Volume of exhaust gases is reduced by 3.5-fold when using combustion in $\text{O}_2$ compared with combustion in air.
Using the equation (5.22), fuel savings were calculated and are shown on Figure 13. In the ideal case, fuel savings of up to 70% are obtained by enriching oxidant.

The rapid increase in available heat and fuel savings that occurs at low enrichment levels proves that this region is of interest. At oxygen concentrations higher than 50%, the gains lower. This proves that membrane separation is fitted to this type of application.

### 5.2.2 Emissions

Figure 14, Figure 15 and Figure 16 show the specific emissions of the three major pollutants as a function of the enrichment level. As the heat retrieved in combustion is increased with O₂ enrichment, the specific emissions (emissions per unit of heat produced) are drastically reduced. That is one major improvement obtained with OEC.
5.3 Case study 1: Oxygen production by membrane

5.3.1 Energetic analysis

As regards the process of membrane separation, membranes with various selectivities were considered, selectivity varying from 3 to 10, which is in the range of available polymeric membranes (Robeson 2008).

For each membrane and level of enrichment, a certain area exists that minimizes the compressor power. Indeed, if mass flow rate through the membrane is fixed, as the area increases, the mass flow by unit area decreases, inducing a reduction of the pressure ratio given by the compressor, as the pressure ratio is governing the flow rate by unit area. Hence, there is a decrease in compressor power. However, when the area increases, the feed flow rate of air in the compressor also increases, which leads after a certain point in which this effect becomes predominant, to an increase in compressor power. Hence there is a minimum power requirement for a certain area. This is illustrated on Figure 17. Figure 18 shows the corresponding turbine power. At the optimum point (defined by the minimum compression power requirement), the turbine power is approximately equal to half of the compressor power.
This area and the associated compressor power were found and considered as the membrane operating point for a given enrichment. Figure 19 and Figure 20 show the compressor power and the areas for various membrane selectivities.

Figure 17 Compressor power as a function of area for various membrane selectivities and for a 26% O2 enrichment

Figure 18 Turbine power as a function of area for various membrane selectivities and for a 26% O2 enrichment

Figure 19 Compressor power as a function of enrichment level for membranes with various selectivities
As can be seen on Figure 19, for a given selectivity, the compressor power increases with the enrichment smoothly until reaching a point where it increases exponentially. After this point, the compressor power is too high to be relevant and it is considered out of operating range. This shows that for each membrane, there is a limited possible level of enrichment, which is higher when the membrane is more oxygen selective. As a consequence, the more selective the membrane is, the better the separation can be achieved. However, as can be seen on Figure 20, the area required also becomes higher for higher selectivities. Thus, a balance should be found between the desired enrichment and the area constraints.

The total energetic efficiency is shown on Figure 21.

As can be seen on Figure 20 Optimum membrane area as a function of enrichment level

Figure 20 Optimum membrane area as a function of enrichment level

Figure 21 System efficiency for various selectivities as a function of enrichment

Figure 21 System efficiency for various selectivities as a function of enrichment
As can be seen on Figure 21, the higher the membrane selectivity is, the higher the maximum efficiency. Compared with combustion with air, the increase in efficiency achievable is significant (from 22% up to 58%). Even for low levels of enrichment, the system efficiency increases rapidly, which makes the membrane process interesting.

**5.3.2 Exergetic analysis**

![Figure 22 System exergetic efficiency for various selectivities as a function of enrichment](image)

Figure 22 shows the system exergetic efficiency as a function of enrichment. The curve was found to be the same for every selectivity, except that the maximum enrichment varies (as shown on preceding figures). The overall exergetic efficiency increases with enrichment as the heat retrieved from the combustion chamber increases.

If all the streams were taken into consideration (that is to say, adding the exergy of the exhaust gases and the exergy retrieved in the cooler), the exergetic efficiency would become equal to 80% and remains almost constant with enrichment (between 78% and 80%) as all the outlet streams would be considered.

Following figures (Figure 23, Figure 24, Figure 25 and Figure 26) show the different exergy rates of destruction and transfer by heat that are affected by enrichment. Three selectivities were chosen (5, 7 and 9). They had an influence only on the exergy destroyed by the membrane and the exergy transfer in the cooler.
Figure 23 shows that, by increasing O₂ concentration in the oxidant, the exergy destroyed in the combustion chamber is reduced. The level of exergy destruction is usually high in any combustion chamber as it comes from the chemical reactions, which are an important source of irreversibilities, and to a minor extent from friction that occurs in the chamber (Bejan, Tsatsaronis and Moran 1996). As can be seen on Figure 23, oxygen enrichment makes this rate of destruction decrease. Exergy transfer by heat is not considered as loss of exergy as it represents the heat transfer to the load, which we intend to maximize. As can be seen on Figure 23, it increases with oxygen enrichment, which is a consequence of the increase of $\dot{Q}_{\text{comb}}$. 
As regards the membrane, there is an increase of destroyed exergy as the feed air is enriched. Despite of this, the exergetic efficiency of the membrane is increased (see Figure 27) as the higher degree of separation provides a proportionally higher availability to the exit streams.

The mixer destroys less exergy as the oxidant is enriched but the proportion of exergy losses is relatively low compared to the other components (around 3-4 kW whereas combustion chamber exergy destruction represents 90 to 115 kW).

Finally, the exergy transferred in the form of heat in the cooler becomes much higher with enrichment. This comes from the fact that higher enrichment requires a higher pressure ratio in the compressor, leading to higher temperatures. When cooling the air to ambient temperatures, all the exergy induced by temperature is destroyed. This term of exergy can be considered as an exergy loss if nothing is done with it. However, it is not considered as a destroyed exergy as it does not come from entropy generation and it could be used in order to preheat another stream for instance.

As regards the turbine and the compressor, their exergetic efficiency is 1, which is the direct consequence of the assumption that the isentropic efficiency is 1. As they are considered as ideal, no exergy is destroyed.

### 5.3.3 Energy transfers and efficiencies

The example of a selectivity 8 was taken for this analysis as it corresponds the selectivity of the presently best polymeric membranes (Burdyny and Struchtrup 2010).

![Figure 28 Compressor power, turbine power and heat retrieved from the combustion chamber as a function of enrichment for a membrane of selectivity 8](image)

Figure 28 Compressor power, turbine power and heat retrieved from the combustion chamber as a function of enrichment for a membrane of selectivity 8
These two figures (Figure 28 and Figure 29) show the various energy flows and efficiencies of the whole system. It can be seen that the maximum efficiency is achieved when enrichment is high, which corresponds to the highest values of compressor power, turbine power and heat. This means that in the case of high efficiency, one has to provide a lot of work in order to retrieve heat power. Depending on the application, this might not be the optimal operating point. If the system objective is to increase the heat to the load in the combustion chamber at the lower price possible, one might prefer a lower efficiency and work in the linear part of the compressor and turbine power (in this case from 22% to 53%) to achieve a higher heat of combustion, without providing such a high quantity of compressor power.

5.4 Case study 2: oxygen production by PSA

5.4.1 Model results

It was shown that varying the operating temperature of PSA had a very small influence on the energetic efficiency and the powers involved (see Appendix C), so it was decided to make the PSA operate at 30°C (lowest temperature for which data of zeolite 5A were available) (Kayser and Knaebel 1986).

In the model simulated, the pressure ratio can be varied. It was decided to use the pressure ratio that would give the maximum efficiency of the system. Figure 30 shows the evolution of the system efficiency with pressure ratio.
Efficiency is maximum when the pressure ratio is $p=3.78$, so this value was chosen.

### 5.4.2 Energetic analysis and efficiency

Table 7 shows the results of the energetic analysis.

<table>
<thead>
<tr>
<th>$x_{O_2}$ [-]</th>
<th>$Rec$ [%]</th>
<th>$W_c$ [kW]</th>
<th>$\dot{W}_t$ [kW]</th>
<th>$\dot{Q}_{comb}$ [kW]</th>
<th>$\eta_{tot}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59.44</td>
<td>32.1</td>
<td>2.79</td>
<td>285.5</td>
<td>66.47</td>
</tr>
</tbody>
</table>

These results suggest that the PSA system has better performance than the membrane one as the compressor work (32.1 kW) is lower than the compressor work required in the membrane case for higher levels of enrichment. Besides, the system efficiency achieved is considerably higher than in the case of the membrane system (66.5% compared to 58%).

The turbine power is very small (2.79kW) and this suggests that the turbine is of no interest in this case and could be replaced by a simple valve, this would reduce the cost of installation, without causing significant efficiency loss (from 66.5% to 65.8%).

The heat retrieved in the combustion chamber is maximum and higher than in the membrane case because the oxidant has been considered to be pure oxygen.

### 5.4.3 Exergetic analysis

#### 5.4.3.1 Streams exergy

Figure 31, Figure 32, Figure 33 and Figure 34 show the exergy levels (both physical and chemical) of the streams at the different points of the system. In the case of membrane, a membrane of selectivity 8 was chosen and an enrichment of 37% $O_2$ (see section 6.6). It can be seen that, at the system outlet, there is still a very high physical exergy (respectively 134.6kW and 74.9kW) due to the gases high temperature at the combustion chamber outlet. This stream could be used for a second process in order to increase the system exergetic efficiency.
Figure 31 Physical and chemical exergy in the membrane system from point 0 to 5

Figure 32 Physical and chemical exergy in the membrane system from point 6 to 8

Figure 33 Physical and chemical exergy in the PSA system from point 0 to 5

Figure 34 Physical and chemical exergy in the PSA system from point 6 to 8
5.4.3.2 Exergy destruction, transfer and efficiencies in the components

The three following figures show the results of a comparative exergetic analysis, considering four different cases: combustion with air, combustion with air enriched at 37% produced by a membrane of selectivity 8 (see section 5.6), combustion with oxidant enriched at 56% by the same membrane (point that corresponds to the system maximum efficiency) and combustion with pure O₂ produced by PSA.

Figure 35 Destroyed exergy of the various components for different modes of operation
Figure 35 shows the destroyed exergy in the various components of interest for the two cycles. The destroyed exergy in the PSA is higher than in the membrane because the pressure given to the PSA columns is lost to make the adsorption process work.
The exergy loss in the mixer is small compared to the other components and the exergy loss is maximum in the combustion chamber as explained before. Due to higher level of enrichment in the PSA system, the destroyed exergy in the combustion chamber for this system is lower.

Figure 36 shows the exergy transfer by heat. It is increased in the combustion chamber with enrichment as seen before. However, the exergy loss in the cooler is high for membranes with high levels of enrichment due to the high compressor power required and so the high air temperature at the compressor outlet. In this case, this heat could be used for another process, increasing the total exergetic efficiency of the membrane system.

Figure 37 shows the exergetic efficiencies. PSA has lower exergetic efficiency than membrane as the pressure that is used in the system is lost in the process. But on a whole, the PSA system has a higher total exergetic efficiency as the efficiency in the combustion chamber is considerably increased by enrichment.

### 5.5 Pollutant emissions: comparison of the two systems

Figure 38, Figure 39 and Figure 40 show the relative specific emissions (=1 when the air composition is 21% O₂) of the three major pollutants for a membrane of selectivity 8.

![Figure 38](image1.png)

**Figure 38** Relative specific CO₂ emissions ignoring the energy consumed by the compressor (eCO₂) and with total energy by the system (eCO₂;tot) for a membrane of selectivity 8 as a function of enrichment.

![Figure 39](image2.png)

**Figure 39** Relative specific CO emissions for a membrane of selectivity 8 as a function of enrichment
As regards PSA, the emissions of pollutants are following the emissions of OEC (Figure 14, Figure 15, Figure 16) because there is almost only production of heat, as the turbine power retrieved is negligible. Besides, for an enrichment level of 100%, the relative pollutant emissions are:

- CO\textsubscript{2}: 30.4\% (32.11\% when considering total emissions).
- CO: 19.33\%.
- NO: no emissions as there is no more N\textsubscript{2} in combustion.

It can be seen on these figures that the oxygen enhanced combustion achieves considerable reduction of pollutant emissions. The reductions achieved with the PSA system are higher as the oxidant is more enriched. The most remarkable result is that even for low levels of enrichment, for instance for 40\% O\textsubscript{2} in the oxidant, specific emissions are reduced of more than 60\%. When considering the emissions of CO\textsubscript{2} associated to the generation of power for the compressor, emissions are higher (Figure 38).

### 5.6 Energy requirements: comparison with cryogenics

According to Kauranen, oxygen production by cryogenics requires between 250 and 450 kWh/ton of O\textsubscript{2} produced (Kauranen 2008). In order to be able to compare with the consumption of membrane and PSA, which only produce an oxygen enriched air, the energy demand of cryogenics was recalculated considering that the oxygen produced by cryogenics would enter the combustion chamber and produce heat. The result is that, it needs between 100 and 180 kWh to produce 1MWh of heat with cryogenics. The same calculations were made for a membrane of selectivity 8 and for various values of enrichment and for the PSA. Results are shown on Figure 41.

For the membrane, it has been chosen to represent the value for the minimum enrichment (22\%) and for the enrichment that corresponded to the maximum work required by cryogenics (37\%).
Figure 41 Energy consumption for the production of 1MWh of heat as a function of the production per day, for various techniques of oxidant production: cryogenics, membrane of selectivity 8 and PSA. Data for cryogenics came from (Kauranen 2008).

Results suggest that the studied techniques could be more interesting than cryogenics for smaller power plants. In the membrane case, 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. As regards the PSA, the process would be better than cryogenics for production up to 3000MWh/day. However, it has to be remembered that the PSA model considered here is idealized, so this would represent an upper limit, the actual size limit being lower in reality.
6 Conclusion

This work has been a proof of concept of two separation systems, polymeric membrane and PSA, applied to oxygen-enhanced combustion. A model for the system and for both processes was developed. Operating curves were found for a polymeric membrane as a function of its selectivity, showing that a high selectivity allows 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.

Separation by Pressure Swing Adsorption was modeled using an analytical solution to the equilibrium model and was shown to be a potentially interesting solution, because energetic and exergetic efficiencies of the whole system increased substantially.

The two systems showed a reduction of specific pollutants emissions, which is one of the major improvements induced by oxygen-enhanced combustion.

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. As regards exergetic efficiency, the membrane showed to have a higher efficiency than the PSA, this last representing a source of exergetic loss in the system. The two processes were shown to be more interesting energetically than cryogenics for small scale production.

Finally, the two systems assessment was based on an energetic and exergetic study, but for a more detailed analysis, an economic analysis should also be done, comparing the two solutions. Besides, the PSA model that was used in this work was based on an equilibrium model, which is an idealized model, as the purity of oxygen out of a PSA system is generally lower (93-95%) with a two-column system. So, the results presented in this work were able to show a limit of PSA performances that could be obtained with a two-bed PSA system working according to the Skarstrom cycle with pressure equalization, but the actual performance would be a bit lower. As a consequence, in a future work, it would be interesting to work on a more accurate model, for instance a model using the linear driving force.
7 List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>membrane area (m²)</td>
</tr>
<tr>
<td>(A_{col})</td>
<td>bed height (m)</td>
</tr>
<tr>
<td>(C_i)</td>
<td>molar concentration of compound i in the fluid phase (kmol/m³)</td>
</tr>
<tr>
<td>(e_i)</td>
<td>specific emissions of compound i (kg/kJ)</td>
</tr>
<tr>
<td>(\bar{e}x_j)</td>
<td>molar exergy at point j (kJ/kmol)</td>
</tr>
<tr>
<td>(\bar{e}x_i^0)</td>
<td>standard chemical exergy of compound i (kJ/kmol)</td>
</tr>
<tr>
<td>(\dot{E}x_j)</td>
<td>exergy at point j (kW)</td>
</tr>
<tr>
<td>(\dot{E}x_k^d)</td>
<td>destroyed exergy at component k (kW)</td>
</tr>
<tr>
<td>(\dot{E}x_k^q)</td>
<td>exergy transfer by heat at component k (kW)</td>
</tr>
<tr>
<td>(F_{savings})</td>
<td>fuel savings (%)</td>
</tr>
<tr>
<td>(\bar{h}_j)</td>
<td>molar enthalpy of the mixture at point j (kJ/kmol)</td>
</tr>
<tr>
<td>(k_i)</td>
<td>equilibrium coefficient for compound i (-)</td>
</tr>
<tr>
<td>L</td>
<td>membrane thickness (µm)</td>
</tr>
<tr>
<td>L*</td>
<td>bed length (m)</td>
</tr>
<tr>
<td>(LHV)</td>
<td>low heating value of CH₄</td>
</tr>
<tr>
<td>(\dot{m}_{i,j})</td>
<td>mass flow rate of compound i at point j (kg/s)</td>
</tr>
<tr>
<td>(N_S)</td>
<td>number of moles entering or leaving the bed in step S (mol)</td>
</tr>
<tr>
<td>(n_i)</td>
<td>number of moles of compound i absorbed per unit volume (kmol/m³)</td>
</tr>
<tr>
<td>(\dot{n}_{i,j})</td>
<td>molar flow rate of compound i at point j (kmol/s)</td>
</tr>
<tr>
<td>P</td>
<td>pressure (Pa)</td>
</tr>
<tr>
<td>(P_{t}, P_{H}, P_L)</td>
<td>pressure after equalization, high pressure and low pressure (Pa)</td>
</tr>
<tr>
<td>(P_i)</td>
<td>permeability to compound i (kmol µm kPa⁻¹ m⁻² s⁻¹)</td>
</tr>
<tr>
<td>(p_{p,i})</td>
<td>partial pressure of compound i (kPa)</td>
</tr>
<tr>
<td>(p_j)</td>
<td>total pressure at point j (kPa)</td>
</tr>
<tr>
<td>(Q)</td>
<td>heat power (MW)</td>
</tr>
<tr>
<td>(R)</td>
<td>ideal gas constant (kJ/kmol.K)</td>
</tr>
<tr>
<td>(r_c)</td>
<td>compression ratio (-)</td>
</tr>
<tr>
<td>Rec</td>
<td>recuperação</td>
</tr>
<tr>
<td>(\bar{s}_j)</td>
<td>molar entropy of the mixture at point j (kJ/kmol)</td>
</tr>
<tr>
<td>(\dot{S}_{gen})</td>
<td>generated entropy (kW/K)</td>
</tr>
<tr>
<td>(T_j)</td>
<td>temperature at point j (K)</td>
</tr>
<tr>
<td>(t_S)</td>
<td>duration of step S (s)</td>
</tr>
<tr>
<td>(u_S)</td>
<td>velocity in step S (m/s)</td>
</tr>
<tr>
<td>(v)</td>
<td>velocity (m/s)</td>
</tr>
<tr>
<td>(V)</td>
<td>total volume (m³)</td>
</tr>
<tr>
<td>(\dot{V})</td>
<td>volume flow rate (m³/s)</td>
</tr>
<tr>
<td>(W_k)</td>
<td>electrical power from component k (MW)</td>
</tr>
<tr>
<td>(x_{i,j})</td>
<td>molar fraction of compound i at point j (-)</td>
</tr>
<tr>
<td>(y)</td>
<td>destroyed exergy fraction (-)</td>
</tr>
<tr>
<td>(y_F)</td>
<td>nitrogen fraction in feed air (-)</td>
</tr>
<tr>
<td>(z)</td>
<td>altitude in the bed (m)</td>
</tr>
</tbody>
</table>

Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>membrane selectivity (-)</td>
</tr>
<tr>
<td>(\beta)</td>
<td>adsorption characteristic constant (-)</td>
</tr>
<tr>
<td>(\epsilon)</td>
<td>exergetic efficiency (-)</td>
</tr>
<tr>
<td>(\epsilon^*)</td>
<td>bed void fraction (-)</td>
</tr>
<tr>
<td>(\eta)</td>
<td>energetic efficiency (-)</td>
</tr>
<tr>
<td>(\Omega)</td>
<td>enrichment (-)</td>
</tr>
<tr>
<td>(\pi)</td>
<td>pressure ratio (-)</td>
</tr>
<tr>
<td>(\varphi)</td>
<td>bed characteristic constant (\varphi = \epsilon^* A_{col} P_L / \beta ART)</td>
</tr>
<tr>
<td>(\phi)</td>
<td>equivalence coefficient (-)</td>
</tr>
</tbody>
</table>

Subscripts
actual real case PO product output
c compressor PR pressurization step
cooler cooler PU purge
comb combustion chamber stoich stoichiometric
cv control volume t turbine
el electrical tot entire system
F feed gases exhaust gases
in inlet CH chemical
memb membrane el electrical
mix mixer PH physical
out outlet tot total

References


Appendix A: Combustion model validation

First, was checked the adiabatic flame temperature. Results are shown on Figure 42.

![Figure 42 Adiabatic flame temperature from (Baukal 1998) and from simulations](image)

Then, the emissions of pollutants were compared under various conditions with the emissions obtained from the computer code Chemical Equilibrium with Application (CEA), which was developed by the NASA.

Results are presented here on Table 8 for the extreme cases: 21% $O_2$ and 100% $O_2$, under stoichiometric conditions.

**Table 8 Comparison of quantity of species formed during combustion between Baukal and the simulation**

<table>
<thead>
<tr>
<th>Species</th>
<th>$21% O_2$</th>
<th>Relative difference</th>
<th>$100% O_2$</th>
<th>Relative difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quantity after combustion in simulations</td>
<td>Quantity found from CEA</td>
<td></td>
<td>Quantity after combustion in simulations</td>
</tr>
<tr>
<td>CO</td>
<td>0.008901</td>
<td>0.00893</td>
<td>-0.32%</td>
<td>0.1553</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.08542</td>
<td>0.08542</td>
<td>0.00%</td>
<td>0.1133</td>
</tr>
<tr>
<td>$H$</td>
<td>0.000386</td>
<td>0.00038</td>
<td>1.61%</td>
<td>0.04923</td>
</tr>
<tr>
<td>$H_2$</td>
<td>0.003566</td>
<td>0.00358</td>
<td>-0.39%</td>
<td>0.07142</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>0.1833</td>
<td>0.18335</td>
<td>-0.03%</td>
<td>0.3908</td>
</tr>
<tr>
<td>NO</td>
<td>0.001848</td>
<td>0.00185</td>
<td>-0.11%</td>
<td>-</td>
</tr>
<tr>
<td>$N_2$</td>
<td>0.7087</td>
<td>0.70858</td>
<td>0.02%</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>0.000211</td>
<td>0.00021</td>
<td>0.33%</td>
<td>0.03816</td>
</tr>
<tr>
<td>OH</td>
<td>0.003193</td>
<td>0.00317</td>
<td>0.73%</td>
<td>0.1003</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.004503</td>
<td>0.00452</td>
<td>-0.38%</td>
<td>0.08144</td>
</tr>
</tbody>
</table>
The chemical equilibrium model is a widely used model for combustion simulations, however there is a slight difference between this model and experimental results. Figure 43 shows the difference in exhaust gases compositions obtained with simulations using a chemical equilibrium model and experimental results for a gas turbine operating at a pressure of 4.1 MPa (it was first shown in the article that the pressure has almost no influence on the exhaust gases composition).

Figure 43  Comparison of components of combustion gases between experimental results and calculations under the pressure of 4.1 MPa. Solid lines mean the results obtained by the theoretical calculations in equilibrium state. Keys are the results by the experiments (Yamamoto, et al. 1997).
Appendix B: Definition of parameters for solving the PSA equilibrium model

This appendix describes the method used to retrieve the different parameters needed for the PSA simulation. The PSA system was modeled for operating between 30 and 60°C.

A linear regression of data from (Kayser and Knaebel 1986) (Table 9) was made to obtain $k_{N_2}$ and $k_{O_2}$ as a function of temperature.

<table>
<thead>
<tr>
<th>Gas</th>
<th>T (°C)</th>
<th>$k_i$ (i=N₂ ou O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>30</td>
<td>9.94</td>
</tr>
<tr>
<td>N₂</td>
<td>45</td>
<td>8.24</td>
</tr>
<tr>
<td>N₂</td>
<td>60</td>
<td>7.55</td>
</tr>
<tr>
<td>O₂</td>
<td>30</td>
<td>5.40</td>
</tr>
<tr>
<td>O₂</td>
<td>45</td>
<td>4.51</td>
</tr>
<tr>
<td>O₂</td>
<td>60</td>
<td>3.723</td>
</tr>
</tbody>
</table>

Results give:

\[
k_{N_2} = -0.0797 \times (T - 273.15) + 12.162 \tag{B.1}
\]

\[
k_{O_2} = -0.0559 \times (T - 273.15) + 7.0598 \tag{B.2}
\]

The parameters $\beta$, $\beta_{N_2}$ and $\beta_{O_2}$ could then be calculated from equations (B.3) and (B.4).

The void fraction $\varepsilon$ was taken as $\varepsilon^* = 0.478$. This parameter does not vary within the PSA operating range (Banerjee, Narayankhedkar and Sukhatme 1989).

The length and area of the PSA column were chosen to be unit arbitrarily. However, in the scope of this study, their value does not influence the results (recovery being independent of them). These parameters could then be arranged to fit with the expected times of each step and cost of the columns.
Appendix C: Results variation with temperature in the PSA system

A comparison was made for operation of PSA at two different temperatures (30°C and 60°C). The results are shown on Table 10.

Table 10 Comparison of the results of PSA for two temperatures of operation (30°C and 60°C). Values were retrieved for the pressure that gave the system maximum efficiency

<table>
<thead>
<tr>
<th></th>
<th>Results at 30°C</th>
<th>Results at 60°C</th>
<th>Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_{rec}$ [%]</td>
<td>59.44</td>
<td>59.06</td>
<td>-0.64%</td>
</tr>
<tr>
<td>$W_c$ [kW]</td>
<td>32.1</td>
<td>34.64</td>
<td>7.91%</td>
</tr>
<tr>
<td>$W_f$ [kW]</td>
<td>2.79</td>
<td>3.22</td>
<td>15.41%</td>
</tr>
<tr>
<td>$Q_{comb}$ [kW]</td>
<td>285.5</td>
<td>286</td>
<td>0.18%</td>
</tr>
<tr>
<td>$\eta_{tot}$ [%]</td>
<td>66.47</td>
<td>66.28</td>
<td>-0.29%</td>
</tr>
<tr>
<td>$Q_{cooler}$ [kW]</td>
<td>30.93</td>
<td>26.42</td>
<td>-14.58%</td>
</tr>
<tr>
<td>$\epsilon_{tot}$ [%]</td>
<td>54.24</td>
<td>54.11</td>
<td>-0.24%</td>
</tr>
</tbody>
</table>
Annex I: Natural gas data

Natural gas is a fuel of growing interest for various reasons. First, the potential for natural gas utilization in Brazil increased in the last years as many new proved reserves appeared (Figure 44).

Figure 44 Natural gas proved reserves in Brazil from 1980 until 2012 (US Energy Information Administration 2012)

This has been followed by an increase in both natural gas production and consumption (Figure 45, Figure 46):

Figure 45 Natural gas production in Brazil from 1980 until 2011
Figure 46 Natural gas consumption in Brazil from 1980 until 2011

Besides, natural gas is considered as a “cleaner” fuel for combustion as its emissions of pollutants are generally lower compared to other fuels (Figure 47).

Figure 47 Average implied CO2 emission factors in the EU (g CO2/MJ) (European Environment Agency 2012)

Natural gas is composed mostly of methane (around 95.2%), the rest being ethane (2.5%), nitrogen (1.3%), carbon dioxide (0.7%), propane (0.2%) and other species in minor quantities (Union Gas 2012).
Annex II: Detailed calculations for the PSA equilibrium model

This annex describes the equations and assumptions made to solve the equilibrium model. Equations were retrieved from (Banerjee, Narayankhedkar and Sukhatme 1989) and (Knaebel and Hill 1985).

Combining equations (3.2) and (3.4), one can get:
\[
\frac{1}{\beta_B} \frac{\partial P}{\partial t} + \frac{\partial}{\partial z} [vP((\beta - 1)y + 1)] = 0
\]

(II.1)

Where:
\[
\beta = \frac{\beta_A}{\beta_B}
\]

(II.2)

\[
\beta_A = \frac{1}{1 + k_A(1 - \varepsilon) \varepsilon}
\]

(II.3)

\[
\beta_B = \frac{1}{1 + k_B(1 - \varepsilon) \varepsilon}
\]

(II.4)

The axial gradient of pressure is neglected in all steps, \( \frac{\partial P}{\partial z} = 0 \). By integrating equation (II.1), the velocity can be obtained for each step.

When the pressure varies (pressurization and blowdown), the composition of the gas phase is assumed to be the same in the whole column so \( \frac{\partial y}{\partial z} = 0 \).

The velocity is then given by:
\[
u = 0 \text{ at } z = 0
\]

And
\[
u = \frac{-z}{\beta_B(1 + (\beta - 1)y)} \frac{1}{P} \frac{dP}{dt}
\]

(II.5)

When the pressure is constant (adsorption and purge), \( \frac{dP}{dt} = 0 \).

The velocity is given by:
\[
u_1 = \frac{1 + (\beta - 1)y_2}{1 + (\beta - 1)y_1}
\]

(II.6)

Where 1 and 2 are two arbitrary points in the column.

The number of moles entering or leaving one column is then calculated for each step.

- Pressure equalization:

Velocity in each bed can be calculated from equation (II.5) considering that \( y = 0 \), given that the beds are connected by their product-end. Equaling the velocities at the end of each bed and integrating this equation between the pressures at the step beginning (one is at higher pressure \( P_H \) and the other at lower pressure \( P_L \)) and the final pressure \( P_f \) which will be the same in the two beds, one can get:
\[
P_f = \sqrt{P_H P_L}
\]

(II.7)
• Pressurization (by product):

The number of moles of product entering the column during pressurization can be calculated by:

\[ N_{PR} = - \int_0^{t_{PR}} u_{PR}(L) \frac{P}{RT} \varepsilon A_{col} \, dt \]  

(II.8)

Where the velocity \( u_{PR}(L) \) is estimated by equation (II.5) considering that pure product enters the column, hence \( y=0 \). At time 0 of this step, pressure is equal to \( P_f \).

The result is that:

\[ N_{PR} = \phi \beta (\pi - \sqrt{\pi}) \]  

(II.9)

• Feed during adsorption:

The number of moles of feed is given by:

\[ N_F = \int_0^{t_F} u_F(0) \frac{P_H}{RT} \varepsilon A_{col} \, dt \]  

(II.10)

Where \( u_F(0) \) is constant at the bed entrance, so:

\[ N_F = - \phi \pi \beta_A u_F t_F \]  

(II.11)

By analyzing the choc wave velocity, it can be shown that \( \beta_A u_F t_F = -1 \).

Hence,

\[ N_F = \phi \pi \]  

(II.12)

• Product output:

As for feed, the number of moles of product leaving the column can be written:

\[ N_{PO} = - \phi \pi \beta_A u_{PO} t_F \]  

(II.13)

Where \( u_{PO} \) is estimated by equation (II.6).

This leads to

\[ N_{PO} = \phi \pi [1 + (\beta - 1) y_F] \]  

(II.14)

• Purge:

As for feed, the number of moles entering the bed from the outlet can be written:

\[ N_{PU} = \phi \beta_A u_{PU} t_{PU} \]  

(II.15)

And it can be shown that \( \beta_A u_{PU} t_{PU} = 1 \).

So,

\[ N_{PU} = \phi \]  

(II.16)

The net product output is the total product output minus the product required for pressurization and purge:

\[ N_O = N_{PO} - N_{PU} - N_{PR} \]  

(II.17)

So recovery can be defined,

\[ Rec = \frac{N_O}{(1 - y_F) N_F} \]  

(II.18)