Recovery of CO\textsubscript{2} from units of Steam Methane Reforming at Sines Refinery

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Abstract

This master degree thesis results from an internship done at Technical Refining Staff of Galp Energia between March and September of 2011 and had as main objective to select the CO\textsubscript{2} recovery process to be applied in hydrogen units located in Sines Refinery.

Initially, was elaborated a general study on the market for liquid carbon dioxide in Europe and particularly in Iberia, being also analyzed the different processes of recovery it with matching industrial existence. Subsequently, were examined the existing two Hydrogen units, as they constitute the source of carbon dioxide.

The comparison of the recovery processes of CO\textsubscript{2}, within this academic analysis, made possible to select the process \textit{FlashCO\textsubscript{2}}, as the one with highest probability of being used in Sines. Then, based up on this process, were estimated the capacities of CO\textsubscript{2} units for extreme conditions, taking into account the utilization rates of hydrogen units concerned. Therefore, it was also completed an analysis of the possible technical and logistical implementation of a CO\textsubscript{2} unit at Sines Refinery.

Finally, an economic analysis allowed to conclude that the CO\textsubscript{2} unit, downstream of the hydrogen production plant HR, is feasible, being the minimum rate of operation below the average of the units in the European Union.

Keywords: CO\textsubscript{2} capture, H\textsubscript{2} production, tail gas, \textit{flashCO\textsubscript{2}} process, Sines Refinery

1. Introduction

Carbon dioxide is normally present at gaseous state (atmospheric conditions) and its presence has been known since the XVI century [1]. Van Helmont was the first to recognize it when he prepared and isolated the gas by various routes: fermentation, action of acids on carbonates, burning of charcoal. Afterwards, Hoffmann discovered that this gas is an acid gas and, Black showed is lethal effect on animal life.

Although, Lavoisier was the first to demonstrate the existence of this gas, when he proved its composition and named it carbonic acid.

The commercial exploitation of carbon dioxide began with attempts to produce
artificial mineral waters and its development was carried on by Faraday and Thilorier, who realized experiments on the liquefaction of gases. Thilorier succeeded in experiments on the expansion, vapor pressure, density, and enthalpy changes of the liquid CO$_2$ during evaporation, and he was the 1st to produce solid carbon dioxide.

The majority of the carbon dioxide generated in the world is a by product of ammonia and hydrogen production. As so, there aren’t processes for production of CO$_2$ and the corresponding raw materials, but there are recovery processes and the sources where the gas can be recovered [1].

Other sources are the flue gases of power plants (natural gas or coal based), cement units and limekilns and in sugar fermentation units like bio-ethanol factories. The last sources of CO$_2$ can be considered as the natural occurrence of the gas in caverns (due to precedent volcanic activity) or the presence in natural gas wells with very high concentrations.

<table>
<thead>
<tr>
<th>Source</th>
<th>Purity (% mol)</th>
<th>Recovery Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen unit</td>
<td>15 - 20 %</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>40 - 50 %</td>
<td>+++</td>
</tr>
<tr>
<td>Ammonia unit</td>
<td>≈ 97 %</td>
<td>+</td>
</tr>
<tr>
<td>Flue Gas from Power plant</td>
<td>10-20 %</td>
<td>+++</td>
</tr>
<tr>
<td>Bioethanol unit</td>
<td>&gt; 80 %</td>
<td>++</td>
</tr>
<tr>
<td>Natural source</td>
<td>&gt; 90 %</td>
<td>+</td>
</tr>
<tr>
<td>Limekilns</td>
<td>≈ 40 %</td>
<td>+++</td>
</tr>
</tbody>
</table>

Nowadays, current uses for CO$_2$ are in the beverage and alimentary industry (higher relevance in Europe), water treatment, enhanced oil recovery (EOR, particularly in the U.S.A.), agriculture, fire extensor and inert agent, metals fabrication industry and chemical application in production of urea and methanol.

2. Market Analysis

The liquid CO$_2$ merchant market was analysed in Portugal, Iberia and Europe.

In Portugal, the liquid CO$_2$ production is only made by Air Liquide in Estarreja. Recently, in 2009, this company made an upgrade of its capacity to 29 kton/year. There were two other units in Lavradio connected to ammonia production, which begun lay-off in 2007 and closed definitely in 2009. Currently, the Portuguese production is around 3,5 kton/year and the consumption about 25-35 kton/year.

In Spain, the liquid CO$_2$ production is made by Praxair, Air Liquide, Linde, Air Products and Neoelectra (decreasing order of capacity), with total production and consumption close to 420 kton/year, being the installed capacity near 693 kton/year.

Therefore, in Iberia the installed capacity is 722 kton/year, from the following sources: hydrogen (57%), ammonia (22%), bio-ethanol (11%) and power plants (10%). The equivalent total consumption is, approximately, 450 kton/year.
In Europe, the merchant of liquid carbon dioxide is around 3600 kton/year, to a corresponding capacity of 5600 kton/year. Here, there is also a production of 1700 kton/year that is stored, in CCS activities.

The sources of CO$_2$ in Europe have a different distribution than in Iberia, being the units of ammonia the main origin (52%), followed by the units of hydrogen (30%) and bio-ethanol (6%). The others sources include CO$_2$ from caverns (Italy, Hungary), from ethylene oxide units (Germany, Belgium) and power plants (Spain, Germany). The European market its controlled mainly by three companies as shown in Figure 2.

![Figure 1 - Geographic location of Refineries and CO$_2$ units in Iberia](image)

![Figure 2 - Market shares by total capacity](image)

3. **H$_2$ production in Sines Refinery**

The hydrogen production in Sines Refinery is carried out by two units: HI of 2003, with a maximum capacity of 30 kNm$^3$ H$_2$/h, and HR from 2011, with 90 kNm$^3$ H$_2$/h [2].

![Figure 3 - HI unit](image)

Both of these units produce H$_2$ by Steam Methane Reforming process, with the main difference in the presence of Pre-Reforming in the case of HR unit [3].

The main advantage of the introduction of Pre-Reforming in the most recent unit is supplied by the savings in the combustion of fuel to fired heater of the SMR, as also the lower production of vapour for export and the higher feedstock flexibility [4].

4. **CO$_2$ capture processes**

The capture of CO$_2$ can be divided in three main categories: pre-combustion, post-combustion and oxyfuelling [5]. In this case, the capture of CO$_2$ from a hydrogen unit is of the first category and is realized in the syngas stream (inlet of PSA) or in the tail gas stream (outlet purge gas form PSA).
The major processes available can be grouped as follows:

- Absorption Processes
- Adsorption Processes
- Membrane Separation
- Cryogenic separation

To remove the CO₂ from the streams mentioned above, all of the process options are viable. However, the capture of CO₂ in Syngas should be done with absorption processes, preferably chemical type (amine MDEA), and in tail gas must be utilized a Cryogenic separation.

4.1. Chemical absorption and MDEA

There are a variety of amines that can be utilized in the treatment of acid gases. To remove of CO₂ at low concentrations, i.e. until 15% of the stream (molar fraction), the most widely used amines is the MEA, DEA and MDEA [5].

The comparison between this amines reveals that MDEA is the most indicated amine to remove CO₂, because it doesn’t react with this gas (so it doesn’t stimulate the corrosion problems), has higher uptake of absorption of CO₂ and requires less energy in regeneration step. As drawback it’s quite more expensive then the others and it can’t react directly with CO₂, so it is necessary a primary dissolution of the gas in water (slow reaction). However, this last disadvantage can be overwhelmed with the addiction of an activator – aMDEA[6],[7].

The MDEA process can even achieve CO₂ removal rates higher than 95% [7].

4.2. Physical absorption

The physical absorption can be utilized when the CO₂ concentration is between 15 and 40% of the stream (molar fraction) and the partial pressure of the gas in the stream is high.

The process bases are quite similar to the chemical absorption with the significant divergence of using a physical agent instead, and that the physical absorption is favoured at low temperatures. As so, the main processes to remove CO₂ are: Selexol (DMPEG), Purisol (NMP), Fluor Solvent (propylene carbonate) and Rectisol process (methanol). The last two processes are the most important and used because their solvents prove to have higher absorption capacities relative to CO₂. Furthermore, the Rectisol has the lowest solvent circulation rate and requires less energy [6].

4.3. Membrane separation

Membrane systems have been particular utilized in the treatment of natural gas with high concentration of acid gases like CO₂. As main advantages, it has higher capacity to adapt to variations of CO₂ in the feed and the spatial requirements of the installation are low [8].

4.4. Cryogenic separation

Cryogenic separation has special utilization in streams where the CO₂ concentration is above 40% (%mol), being ideally to remove CO₂ from tail gas stream.

This separation path includes the following operations to obtain CO₂:
compression, cooling, expansion and distillation (to higher purity requirements). The main disadvantages of these processes are related to the conditions of operation: high pressure and low (negative) temperatures. These conditions are supported by the necessity of working near the triple point of CO\textsubscript{2}: -56ºC and 5.2 bar.

The three main processes are: *FlashCO\textsubscript{2}* process of Union Engineering, CO\textsubscript{2}-CPU of Air Liquide and CO\textsubscript{2}LDSep of Fluor.

The advantages of *FlashCO\textsubscript{2}* over the other cryogenic process are the lower energy consumption presented, near 350 kWh/ton of CO\textsubscript{2} compared with at least 420 kWh/ton of CO\textsubscript{2}, the lower pressure conditions (with total pressure bellow 30 bar) and the higher capacity of CO\textsubscript{2} removal - 90-95% compared to 60-85% (CO\textsubscript{2}LDSep) and 80% (CO\textsubscript{2}-CPU) [6] [9].

Therefore, the *FlashCO\textsubscript{2}* process represents a viable method of removing CO\textsubscript{2} with lower operation costs and possible increase of H\textsubscript{2} production.

The referred process begin with compression and liquefaction of the tail gas to produce a first stream rich in CO\textsubscript{2} (that includes 50-70% of all the CO\textsubscript{2} present in the tail gas) which is send to a distillation column to purification (inlet of 95% purity and outlet with food and beverage grade CO\textsubscript{2} – purity above 99.5%). The gas stream (originated on the liquefaction section) has the remaining CO\textsubscript{2} and is send to a selective absorption unit where methanol is used as physical agent. The methanol absorption increases the CO\textsubscript{2} removal rate and produces a stream of off-gas (mainly composed by H\textsubscript{2}, CO, CH\textsubscript{4} and residual CO\textsubscript{2}) that can be send to a PSA or membrane unit for H\textsubscript{2} recovery.

5. Process Selection

The option of capturing the stream of Syngas is technically more difficult to implement for units that did not consider this option at the time of its construction, since there is space or utilities constraints that turn the plant unfeasible. For instance, one of the biggest limitations is reflected in changing the configuration of the unit, given that the stream of *Syngas* (PSA inlet) would then have a quite different composition (with higher H\textsubscript{2} purity) and lead to critical modifications in quantities of PSA adsorbents.

As so, the capture must take place after the PSA, since that’s the option that will least disturb the normal operation of either one of the hydrogen units in Sines Refinery.

The option for *FlashCO\textsubscript{2}* process was made taking into consideration the source of capture and the best available techniques in the industrial sector. Therefore, the main advantages considered were the lower energy consumption and the higher capacity for CO\textsubscript{2} removal.

The choice of the hydrogen unit where to implement a CO\textsubscript{2} recovery plant was based mainly in a technical and logistical analysis, that revealed the presence of spatial restrictions (area available is insufficient) and lack of direct access to...
utilities (not enough power at the nearest substation) in the HI.

Therefore the recovery should take place downstream the HR unit, since this unit isn’t affected by the same of constraints of HI unit and since this unit allow possible expansion of the CO₂ unit in the future.

6. Plant implementation

The standard operation parameters and conditions can be observed in the Figure 4, being the feed at low pressure (from 0,2 to 2 bar) [10].

Next, were investigated the possible consequences of the integration of this unit in the regular functioning of HR unit and the Sines Refinery itself.

As result, was discovered that changes in raw material of the HR won’t affect dramatically the composition of the tail gas, unchanging the operation of the CO₂ unit. Furthermore, it was recognized that the burning of the off-gas (H₂ rich stream) can’t be a recommendable action as the design of the burners in the Top-Fired Steam Reforming doesn’t account for the higher percentage of H₂ verified and, consequently, this stream must have another destiny: refinery fuel gas stream or H₂ recover by membranes system + PSA, for instance [11].

In the other hand, it was calculated a possible maximum CO₂ emission reduction around 50 to 70 ktons per year (between 2,8 and 4% of total CO₂ emissions by Sines Refinery).

Figure 4 – Generic block diagram of a CO₂ unit with FlashCO₂ process
7. Economical Analysis

To complete this macro analysis about a possible installation of a CO$_2$ capture unit in Sines Refinery, it was imperative to make an estimation of the investment required, taking into consideration investments in similar units. In addition, it would be important to analyze the costs of CO$_2$ capture both in terms of utilities and solvents (variable costs), as well as maintenance, land use and workforce (direct and fixed costs) and product distribution (transport).

The investment required to build this CO$_2$ capture plant will be around 11.5 to 14.5 M€ (for a range of capacity between 50 and 70 kton/year) and was calculated by comparison with other similar investments in units with the exact same process and constraints [12].

![Figure 5 - FlashCO$_2$ recovery unit in Chile](image)

The CO$_2$ capture cost (only utilities and solvents considered) was determined by the average of the examples available, as being around 22.9 € per ton of CO$_2$ recovered.

The total direct and indirect costs (utilities and solvents plus maintenance, raw material, patent, etc) were estimated from 41.1 to 39.7 €/ton of CO$_2$ recovered (increasing the plant capacity). In the other side, the fixed costs are between 7.1 and 6.4 € per ton of CO$_2$ recovered.

Relatively to distribution sector, it was verified that, although the cost would be lower for ships and rail system, due to the lower investment required and the characteristics of the customers (minor individual consumption), the road transportation becomes the preferable option. Therefore, the transportation cost calculated was around 20.8 €/ton of CO$_2$ until a maximum radius distance of 200 km (exponential increase from that point on).

To determine the margin for the CO$_2$ price outside the HR unit (tail gas stream), it was necessary to calculate, historically, the selling price of the product (CO$_2$ pure liquefied), knowing that it’s inside a volatile market where the transport and raw material cost have huge influence.

The economic viability of CO$_2$ recovery unit was analysed with the calculation of the break-even point and other economic indicators, such as the TIR, the VLA and the RP.

<table>
<thead>
<tr>
<th>Economic indicators</th>
<th>HR (X kton)</th>
<th>HR (Ykton)</th>
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</thead>
<tbody>
<tr>
<td>Break-even point (% of unit capacity)</td>
<td>74%</td>
<td>65%</td>
</tr>
<tr>
<td>V. A. L. (M€)</td>
<td>11.749</td>
<td>23.264</td>
</tr>
<tr>
<td>T. I. R. (%)</td>
<td>13.1%</td>
<td>17.5%</td>
</tr>
<tr>
<td>R. P. (years)</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>
8. Conclusions

The market analysis revealed the potential for the installation of a new CO$_2$ recovery unit in Iberia.

The specifications of CO$_2$ recovery and transportation made the introduction of a unit in Sines Refinery possible, being abruptly promoted if any of the Ammoniac factories shutdown.

On the other hand, the sensitivity analysis revealed the importance of the cost of the product distribution and the raw material price, within total cost. Deviations of these parameters exposed that the distance distribution of the product is vital to the profitability of the unit, overriding the effect of increasing raw material price.

In summary, with this work, it can be conclude that the integration of a carbon dioxide recovery unit should be performed downstream of the hydrogen production unit HR (Refinery Plant III), if the market allows the unit to operate above the break-even point and preferably if there’s a guarantee that the sales of product are made continuously on a contractually trade arrangement.

9. References


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