# POLITECNICO DI TORINO

### Master degree in Energy and Nuclear Engineering

## Master thesis

# AUTOTHERMAL REFORMING PLANT WITH CCS: TECHNO-ECONOMIC INVESTIGATION



## Supervisor

Prof. Pierluigi Leone

Candidate

Andrea Rovere

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### Abstract

This thesis addresses a techno-economic assessment of an autothermal reforming plant to produce hydrogen integrated with a carbon capture system. Natural gas mixed with steam (ratio of 1.5 [molH2O/mol CH4]) reacts in a Nickel-based catalyst reformer to produce syngas with a H2/CO ratio of 2.9 [mol/mol]. Heat request by the reaction is provided by the combustion of a part of natural gas fed to the reformer by feeding pure oxygen. Oxygen is produced by a cryogenic separation of air and supplied to reformer with a O2/C ratio of 0.6 [mol/mol]. CO contained in syngas produced is converted in CO2 thanks to water gas shift process leaded at two different temperatures. Carbon capture technology is based on MEA scrubbing, which allows to capture 90% of CO2 with a consumption of 3.8 [GJ/tCO2]. Throw a PSA unit, 90% of H2 is separated by scrubbed gas exiting from MEA capture system. Remaining gases are supplied to a furnace where They are burned to produce heat available to external steam power cycle. To have a better comparison, the plant is compared with a SMR plant with CCS system, because It represents the state of the art of commercial hydrogen production. A detailed techno-economic comparison is conducted. Both plants are simulated by use of Aspen HYSYS v8.8 software. Economic results are based on discounted cash flow analysis (DCF). At the end of the study, a LCOH of 1.86 [USD/kg] for ATR is obtained respect with 1.67 [USD/kg] of SMR plant. Moreover, minimum hydrogen selling price founded is 2.27 [USD/kg] for ATR case and 1.79 [USD/kg] for SMR one, which takes in account all revenues, expenses and taxes. Analysis is conducted with a discount rate of 10% due to higher risk respect with traditional plant. A sensitivity analysis is also conducted to understand how cost changes influence the final gas production cost. Carbon tax effect has been investigated in the range of 0-100 [ $\xi$ /t].

Results show that autothermal reforming represents a valid alternative to SMR plant, because only a contained increment on hydrogen production occurs parallel to a significant increase in CO2 capture capacity. However, economic results show the importance on possible future incentives from environmental politics.

# INDEX

1	Ger	neral Introduction	12		
2 Concepts for hydrogen production plant with carbon					
С	apture	and storage	18		
	2.1	Carbon capture and storage overview	19		
	2.1.	1 Carbon dioxide capture technologies	21		
	2.1.	2 Carbon dioxide transport	25		
	2.1.	3 Carbon dioxide storage	26		
	2.2	Pre-reforming of natural gas	30		
	2.3	Natural gas reforming technologies overview	32		
	2.4	Water-gas shift process	35		
	2.5	Hydrogen separation process	36		
	2.6	Advanced natural gas reforming technologies	37		
3	Me	thodology and Assumptions	40		
	3.1	The choice of plant technology	40		
	3.2	Assessment of a possible location of the plant	42		
	3.3	Plant description	47		
	3.3.	1 Air separation unit	49		
	3.3.	2 Pre-reformer and autothermal reformer section	49		
	3.3.	3 Water gas shifting section	51		
	3.3.4	4 Carbon dioxide capture section	52		
	3.3.	5 Hydrogen purification section	55		
	3.3.	6 Exhaust gas recovery section	56		

3.4	Те	chnical assumptions	56
3.4	4.1	Plant capacity	56
3.4	4.2	Plant location	57
3.4	4.3	Capacity factor	58
3.4	4.4	Input Specifications	58
3.4	4.5	Product specifications	60
3.5	M	odel simulation	60
3.6	Pe	rformance indexes	61
3.7	Re	ference plant	64
3.8	Se	nsitivity Analysis	66
3.9	Ec	onomic assumptions	67
3.9	9.1	Financial structure	67
3.9	9.2	Operation and maintenance costs	70
3.9	9.3	Definition of economic structure	72
3.9	9.4	Capital cost investigation	76
4 Re	sults	5	81
4.1	Те	chnical results	82
4.1	1.1	Technical comparison	84
4.2	Ec	onomical results	86
4.2	2.1	Economic comparison	90
4.3	Se	nsitivity Results	93
5 Cc	ost co	omparison	96
6 Cc	onclu	sions	98
7 Re	efere	nces	101
	3.4 3.4 3.4 3.4 3.4 3.5 3.6 3.7 3.8 3.9 3.9 3.9 3.9 3.9 3.9 3.9 3.9 3.9 3.9	3.4 Te 3.4.1 3.4.2 3.4.3 3.4.4 3.4.5 3.5 Mo 3.6 Pe 3.7 Re 3.8 Se 3.9 Ec 3.9.1 3.9.2 3.9.1 3.9.2 3.9.3 3.9.4 4 Results 4.1 Te 4.1.1 4.2 Ec 4.1.1 4.2 Ec 4.2.1 4.3 Se 5 Cost cc 6 Conclu 7 Refere	<ul> <li>3.4 Technical assumptions</li> <li>3.4.1 Plant capacity</li> <li>3.4.2 Plant location</li> <li>3.4.3 Capacity factor</li> <li>3.4.4 Input Specifications</li> <li>3.4.5 Product specifications</li> <li>3.4.5 Product specifications</li> <li>3.5 Model simulation</li> <li>3.6 Performance indexes</li> <li>3.7 Reference plant</li> <li>3.8 Sensitivity Analysis</li> <li>3.9 Economic assumptions</li> <li>3.9.1 Financial structure</li> <li>3.9.2 Operation and maintenance costs</li> <li>3.9.3 Definition of economic structure</li> <li>3.9.4 Capital cost investigation</li> <li>4 Results</li> <li>4.1 Technical results</li> <li>4.2.1 Economic comparison</li> <li>4.3 Sensitivity Results</li> <li>5 Cost comparison</li> <li>6 Conclusions</li> <li>7 References</li> </ul>

### LIST OF TABLES

Table 1: CO2 emissions from different fossil fuels source to hydrogen
production reported by S. Bourne [3]15
Table 2: Summary of CO2 separation technology    25
Table 3: Optimum values for proven WGS processes
Table 4: Main input values to pre-reformer and ATR reformer51
Table 5: Input values to WGS section51
Table 6: Reference parameters to simulation of CO2 process54
Table 7: Performance parameters to PSA simulation
Table 8: List of main assumptions related to plant location
Table 9: Natural gas composition of Algeria used in the simulation59
Table 10:Range of selected costs to investigate a sensitivity analysis 67
Table 11: Main fixed and variable O&M economic assumptions         71
Table 12: Definition of an economic structure related to the plant
studied (An investor/owned utility structure was chosen)72
Table 13: In the table are reported the coefficients chosen to find pump
costs. Centrifugal pumps made of stainless-steel material are selected
[35]
Table 14: List of economic assumptions related to different plant
sections to calculate entire plant cost79
Table 15: Economic structure adopted to calculate total overnight cost
(TOC)80
Table 16: Main properties and composition of major streams derived
from software simulation related to overall system (composition is
reported in mol%)81
Table 17: Main properties and composition of major streams related to
CO2 capture system simulation (composition is reported in mol%)82
Table 18: List of all general inputs, outputs and technical indexes       83
Table 19: List of CO2 capture system simulation results
Table 20: Economic results of the plant87
Table 21: Calculation of TASC during expenditure period88
Table 22: O&M costs

#### LIST OF FIGURES

Figure 1: The figure reports CO2 emissions trends for 2DS and B2DS
scenarios and the total reduction of emissions which should be adopted
by 2060 to achieve climate targets [2]12
Figure 2: Contributes to hydrogen production from different sources [5]
Figure 3: Scheme of different capture processes: (1) post-combustion
capture, (2) pre-combustion capture and (3) oxyfuel combustion [7] 19
Figure 4: The chain of carbon capture and storage (CCS) [7]21
Figure 5: Schematic CO2 chemical absorption capture from syngas
(Source: https://www.jisf.or.jp/course50/tecnology02/index_en.html) 22
Figure 6: Different options of CO2 storage [8]
Figure 7: ATR-reformer view [10]34
Figure 8: Schematic summary of advanced technologies to produce
hydrogen [5]
Figure 9: Chemical looping cycle [5]
Figure 10: The figure helps to understand the exact disposition of natural
gas field and pipeline in Algeria's country (source: http://energy-
cg.com/OPEC/Algeria/Algeria_OilGas_Industry.html)44
Figure 11: General scheme of the plant with main inputs and outputs48
Figure 12: Scheme of general financial structure adopted by NETL68
Figure 13: Different contributes to LCOH90
Figure 14: Contributes to overall capital plant cost91
Figure 15: List of contributes to OPEX in case of ATR plant
Figure 16: List of contributes to OPEX in the reference plant case93
Figure 17: Range of LCOH according to natural gas cost variations94
Figure 18: Range of LCOH according to electricity cost variations94
Figure 19: Range of LCOH according to CCS cost variations
Figure 20: Effect of "Carbon tax" on LCOH95

### 1 General Introduction

It was 1975, when the well-known expression "Global warming" was introduced in the article of Wallace Broecker "Climatic Change: Are We on the Brink of a Pronounced Global Warming?" published by "Life" journal. It was a fundamental starting point to account more importance about the problem of climate change. In December 2015, 195 countries have adopted Paris Agreement which is a long-term agreement on climate goals. At 2050, climate targets of 2 [°C], corresponding to 2 [°C] scenario (2DS), and "well below" 2 [°C], corresponding on Beyond 2 [°C] Scenario (B2DS), was defined. In this way, knowing the horizontal time, an estimation of total greenhouse emissions is possible [1]. A report of "Global CCS Institute" states that, with actual emissions, 2 [°C] target will be overpassed in 20 years with a 50% of probability [1].



Figure 1: The figure reports CO2 emissions trends for 2DS and B2DS scenarios and the total reduction of emissions which should be adopted by 2060 to achieve climate targets [2]

At 2014, global primary energy demand mix was composed by oil (32%), coal (29%), natural gas (21%), biomass and waste (10%), nuclear (5%) and renewables (3%) with a total energy demand of 570 [EJ] [2].

Referring to 2DS scenario, a growth in primary energy demand of 17% will be expected in 2060, when renewables will dominate the energy mix with a share of 52% [2], while fossil fuels consumption will be 50% lower than 2014 level [2].

Global final energy demand, which is the energy consumed by end-use sectors such as transport, buildings, industry and agriculture, was 402 [EJ] in 2014 [2]. It was satisfied by oil (39%), electricity (18%), coal (15%), natural gas (14%), biomass and waste (10%) and commercial heat (3%) [2]. In the 2DS scenario, the composition of final energy use will be principally accounted by low-carbon energy with an important decline to 22% (oil) and 6% (coal), while only a slightly decline to 13% will be achieved regards to natural gas share [2].

At 2014, CO2 emissions from energy sector were principally caused by power (40%), industry (24%), transport (22%) and buildings (8%) [2]. In the 2DS scenario, these emissions should be reduced at a quarter of 2014 levels by 2060 [2]. Objective of European union is the reduction of 80-95% by 2050 compared to 1990 levels [3]. As we can see, the future will be marked by a substantial reduction of greenhouse emissions with the scope to achieved severe climate targets. The major role in cumulative CO2 emissions reduction will be leaded by more efficient system and renewable energy with shares of 40% and 35% respectively [2]. A promising solution is represented by carbon capture and

storage (CCS), which will bring to a reduction of CO2 emissions of 14% in 2DS scenario prevision [1]. To achieve a sustainable energy future, fossil fuels should be substitute with renewable sources or provide a sequestration of CO2 emission derived from fossil fuels combustion. Recently, more and more attention towards hydrogen as energy carrier is increased. The growing interest about hydrogen is principally caused by two aspects [3]:

- No greenhouse emissions or air pollutants from Hydrogen combustion;
- Production from a variety of low-carbon sources: renewable electricity, biomass, nuclear and fossil-fuels, if the last ones are equipped by CCS system;

Hydrogen will play an important role in the future, because It can be a flexible alternative to electricity. In fact, there are several emissions sources in which energy demand is substantially covered by fossil fuels and an electricity employment is very difficult to obtain [3]. Examples are: iron and steel production, heat for buildings, high-temperature industrial heat, longdistance transport and so on [3]. So, these citated emissions could be reduced by the use of hydrogen, because It represents a valid free-emission alternative to natural gas, oil and coal [3]. Hydrogen and electricity are two energy carriers much similar between them which can be employed in many applications and both of them can be produced from a large variety of sources [3]. Nowadays the reforming of hydrocarbon covers 96% of the total hydrogen produced and the other part comes from electrolysis [4]. More in detail, the reforming of natural gas covers 48% [4] of the hydrogen production, while oil-based production and coal gasification contribute to 30% and 18% of the total reforming of fossil fuels respectively [5]. Depending on different sources, hydrogen production emissions have different values, which are reported in the table below.

Hydrogen produced from:	Emissions [kgCO2/kgH2]		
Natural gas	10		
Oil	12		
Coal	19		

Table 1: CO2 emissions from different fossil fuels source to hydrogen
production reported by S. Bourne [3]

Concerning to the hydrogen production from water electrolysis, just a minor part of the total hydrogen is produced, due to the higher costs rather than other technologies. Moreover, in the last years, costs of solar and wind power are highly decreased causing lower renewables electricity costs [3]. So, a cost reduction of electrolytic hydrogen was observed and, in the future, It could play an important role to decarbonise the energy production.

To recognise the origin of hydrogen produced, hydrogen was associated to different colours. The most important are "Blue" and "Green" hydrogen. "Blue" refers to hydrogen produced from fossil fuels with CCS system to reduce CO2 emissions, while "Green" hydrogen refers to hydrogen produced from renewable electricity [3].

Gaseous Hydrogen produced can be injected into natural gas pipeline to be transport over very long distances. Recently, "SNAM" society has carried out a test of hydrogen injection in Italian natural gas grid in the province of Salerno. A mixed hydrogen-natural gas at 5% was used. If this percentual is applied to entire natural gas volume transported in the Italian grid, 3.5 billion of  $[m^3]$  of hydrogen could be injected with a potential reduction of 2.5 [Mt/year] of CO2. According to a recent study of "Navigant consulting society", promoted by "Gas for Climate", Europe has a potential of 170 billion of  $[m^3]$  of Hydrogen useful to decarbonise energy scenario with an important cost recovery respect with only natural gas-based scenario. Jorgo Chatzimarkakis, general secretary of "Hydrogen Europe", states that: "Italy has the potential to become hydrogen European hub in the next years, because It's equipped by more extended gas grid of the Europe and It represents the bridge towards North Africa, where, in the future, will be produce the most part of green hydrogen from solar energy".



Figure 2: Contributes to hydrogen production from different sources [5] In the near future, as mentioned above, hydrogen production will be principally extracted from fossil fuel. Natural gas

reforming will be the best way to produce hydrogen generating significative CO2 emissions [3]. Fossil fuels employment to hydrogen production causes an amount of CO2 emissions of 500 [Mt/year] approximately [5]. To coupling a sustainable hydrogen production with a deep reduction of CO2 emissions, reforming plants based on fossil fuels should be equipped with a CCS system [2]. In the 2DS scenario, CCS will be extensively used in power and industry sector to achieve an emissions reduction of 14% [2]. At 2018, "Global CCS Institute" states that 21 carbon capture plants operate with a CO2 capture capacity of 37 [Mt/year] [1]. Moreover, to achieve Paris' agreement on climate change, 2500 plants should be in operation at 2040 [3]. Around the world there are some existing demonstration projects to allow a CCS technology development. In this way, some technoeconomic information and operation experience are provided to understand better the feasibility of a determined technology associated to carbon capture process. In the Port Arthur project, leaded by "Air Products" company, an existing SMR plant is retrofitted with an advanced CO2 capture technology based on vacuum swing adsorption (VSA) [6]. The plant is designed to capture more than 90% of CO2 before the PSA process [6]. From a joint venture among "Shell Canada Energy", "Chevron Canada Limited" and "Marathon Oil Canada Corporation" grow Quest Project, where a CCS system is integrated with a hydrogen production plant based on SMR technology [6]. All the CCS system, from capture to injection phase, is monitored to provide a complete experience [6]. Carbon capture process comes before the PSA process and It is based on the Amine scrubbing [6]. In Port Jerome ("Air Liquide") and Tomakomai ("METI of Japan") projects, CO2 capture derives from gases exiting from PSA process [6]. In the Tomakomai Project, carbon capture is based on amine absorption at a rate of 100,000 [t/year], which are transported at the injection point throw a pipeline [6]. In the Port Jerome Plant, a cryogenic separation system, developed by "Air Liquide", is involved to capture CO2 from PSA tail gas at a rate of around 300 [t/d] [6].

In the light of these aspects, this study will study the real feasibility a reforming plant equipped with a section to remove CO2. The plant will be analysed on technical and economic aspects. In particular, the most important result will be the cost of hydrogen produced to understand how much the higher costs caused by CCS system will modify the final cost. At the end of the study, results will be compared with actual market hydrogen cost and commercial plant to produce hydrogen to understand better the feasibility of the plant selected.

# **2** Concepts for hydrogen production plant with carbon capture and storage

This chapter reports a general description of technologies involved in the plant, presenting all the possible options available to our plant. In the first part, a detailed description on CCS chain is provided followed by all reforming technologies to produce hydrogen. By the way only mature technologies will be employed in the plant, a brief description of emerging technologies will be provided to have a detailed overview on reforming and capture technologies.

### 2.1 Carbon capture and storage overview

CCS is a process composed by capture, transport and storage of carbon dioxide and every step will be descripted in the next paragraphs. Starting from the first step, there are some CO2 capture methods, which can be classify in:

- Pre-combustion capture
- Post-combustion capture
- Oxyfuel combustion



Figure 3: Scheme of different capture processes: (1) post-combustion capture, (2) pre-combustion capture and (3) oxyfuel combustion [7]

In case of fossil fuels reforming to produce Hydrogen, precombustion capture process is employed. A syngas, composed by carbon monoxide and hydrogen principally, is produced from methane reforming with water vapour. Before CO2 removal, syngas and water vapour react to oxidise CO in CO2 and to produce more H2 thanks to water gas shift step. So, we obtain a gas stream with higher concentration of CO2 which can be captured thanks to a capture process. On the contrary, postcombustion capture process removes CO2 directly from flue gases produced by fossil fuels combustion. In general, low CO2 partial pressure in flue gases bring to use chemical absorption system based on amine solutions principally. In case of oxyfuel combustion, an air separation unit produces an oxygen stream at high purity to be used in fossil fuel combustion. In this way we can obtain a flue gases stream composed by CO2 almost entirely. These systems have higher capture efficiency, but they also present disadvantages as air separation costs and technological problems to the compressors and turbines. The chain of CCS starts from capture of CO2, which represents the most energy and expensive process. In fact, in this step CO2 capture, purification and compression occur. Today different capture technologies exist, but the most used are absorption, adsorption and low temperature processes. A great variety of solvent materials are available on the market such as amines, activated carbons, zeolites, alkali, ionic liquids and so on [7]. Some criteria are important to select an optimal solvent such as low cost, good regeneration and long-term stability other than a high CO2 sorption capacity [7]. After that, CO2 captured reach the storage site by existing pipeline where, thanks to underground injection, It will be permanently stored. A scheme of entire carbon capture and storage chain with relative options is reported in the figure below.



Figure 4: The chain of carbon capture and storage (CCS) [7]

### 2.1.1 Carbon dioxide capture technologies

The most commercial mature technology to separate CO2 from a gas mixture is the absorption process. More in detail, in an absorber column the contact between gas and liquid solvent allows to remove CO2. Two streams exit from column: a stream of purified gas and another composed by solvent and CO2 captured to regenerate. In another column, named stripper, regeneration is obtained after rich solvent heating. At the top, after water separation, a CO2 stream at high purity is obtained. Liquid solvents can be chemical or physical. Chemical solvents are principally based on amines such as mono-ethanol amine (MEA) and mono-di-ethanol amine (MDEA) [7]. In the process, amines react with CO2 and They are regenerated thanks to an important amount of heat. Moreover, Amines offer high reaction rate and small section size [5]. Physical solvents require less energy than chemical ones and they are principally used in the Rectisol, Selexol and Purisol technologies [5], which employ methanol, glycol and n-methyl-2-pyrolidone solvents respectively [7]. In the physical absorption, according to Henry's law, low temperature and high pressure favour CO2 capture and, therefore, this type of process is preferred in case of high CO2 partial pressure [7]. On the contrary, at low CO2 partial pressures, chemical absorption presents relatively high absorption capacity until reaching the saturation to a certain value of CO2 partial pressure [5]. For example, the purity of CO2 obtained from MDEA syngas separation process is major than 99% satisfying transport criteria set to 95% [5]. Concerning to the removal capacity, values higher than 90%, as in the case of syngas from ATR reported by M.Voldsund et al. in [5], are obtained.



Figure 5: Schematic CO2 chemical absorption capture from syngas (Source: https://www.jisf.or.jp/course50/tecnology02/index\_en.html)

Carbon dioxide separation can be also obtained throw adsorption process. It is based on a physical process that fixes molecules of CO2 over a surface made of adsorbent material. The process takes advantage from different affinities between gas to separate and types of adsorbents [5]. Pressure swing adsorption (PSA), vacuum swing adsorption (VSA) and temperature swing adsorption (TSA) are the most promising adsorption processes for CO2 capture [5]. From commercial point of view, PSA is widely employed to selective removal of CO2 from the syngas [7]. High pressure syngas stream from reforming section entering in the PSA unit and the selective adsorption of CO2 is obtained throw a series of pressurization and depressurization cycles over some adsorbent beds [7]. At the end of the process, a CO2 depleted syngas exits from adsorption unit at low pressure, while rich CO2 stream has to be regenerated from adsorbent bed. Moreover, the purity of CO2 from PSA separation is not sufficient to transport and storage option and another separation process has to be employed [5]. An example is reported by M. Voldsund et al. [5] where, thanks to an addition of a VSA process between SMR and PSA existing unit, more than 90% of carbon dioxide was captured with a purity higher than 97%. The most used adsorbent materials are activated carbons and zeolites [7]. Recently, thanks to a very high porosity, metal oxide framework (MOF) and nanostructured carbon-based sorbent materials allowed to increasing CO2 adsorption capacity [7] and so a more intensive research is conducted.

In case of low temperature separation, CO2 can be separated from other gases with higher boiling point throw a physical separation during cooling phase. Generally, syngas derived from coal and natural gas have CO2 partial pressure lower than CO2 triple point pressure that favour vapour-liquid separation [5]. CO2 captured is in liquid state and so It is an advantage to transport both by ship and pressurization or to transport in pipeline, because It requires less compression energy. Tokyo Gas plant, in Japan, is an operating plant with low-temperature CO2 sequestration and It allows to remove 90% of CO2 with an overall reduction plant efficiency from 81.6% to 78.6% [5].

CO2 can be also separated by membranes. They have different selectivity towards different gas species causing separation. Gas that crossing the membrane is named permeate, while gas not filtered is called retentate [5]. Polymeric and inorganic membranes are the principal technologies [7]. Polymeric membranes are relatively economical with an efficient CO2 separation, but they also present degradation at high temperature [7]. Inorganic membranes are more resistive in corrosives ambient and with high temperatures, but they are also more expensive. They are largely employed in CO2 separation [7]. Major challenges are high stability and low cost, which should be solved to allow a membrane employ in large-scale plants [5]. Moreover, carbon dioxide presents bigger molecular size that causing a lower efficiency of separation and so a less research about CO2 membrane [5].

Process	Adsorption	Absorption	Absorption	Membrane	Low temperature
Technology	(VSA)	physical	Chemical (MDEA)	(Pd-based)	CO2 capture
CO2 purity (mol%)	>97	95-99.7	99.9	Low	99.7-99.9
CO2recovery (%)	>90	90-97	95	High	85-90
reference	[5]	[5]	[5]	[5]	[5]
syngas from:	SMR	Gasified coal	Air-blown ATR	SMR	Gasified coal

Table 2: Summary of CO2 separation technology

### 2.1.2 Carbon dioxide transport

When CO2 captured have to be transported in a different site, It is necessary to reduce its volume throw different options such as compression, liquefaction, solidification and hydration [7]. From a technological point of view, CO2 transport in compressed and liquefied form is the mature choice of transport, while other options are in phase of research [7]. Depending on particular state, CO2 can be transported by pipelines, ships and tanks [7]. The CO2 capture technology used in the hydrogen production plant influences the choice of the transport mode. In particular, when amine scrubbing is used, CO2 is compressed to 135 [bar] and transported towards storage site thanks to pipelines [7]. Global existing CO2 pipeline infrastructures covers around 6,000 [Km] with a transport of 50 [Mt/year] of CO2 from industrial sources to enhanced oil recovery site [7].

### 2.1.3 Carbon dioxide storage

Carbon dioxide storage options represent a great challenge, because they will have to guarantee CO2 encapsulating over very long period. It represents the final step in the CCS chain. In the near and medium term, geological storage represents the principal technology to CO2 sequestration [7]. Nowadays, the most storage option considered is represented by saline aquifers, because They are able to storage enormous quantity of CO2 thanks to their potential storage volume [8]. A negative aspect of storage in saline aquifers is from an economical point of view. In fact, the entire infrastructure to inject CO2 underground, such as injection wells and pipeline, has to be built. Generally, saline aquifers are on a depth higher than 1 [km] and in correspondence of sedimentary basins. It's very important that caprock of these basins has very low CO2 permeability to assure an efficient CO2 containment without losses towards atmosphere [8]. In fact, CO2 supercritical inside the saline aquifer has a density lower than density of saline water and so CO2 rises up. Inside the reservoir, CO2 begins to react with gas, water and rocks. So we can have a formation or dissolution of minerals which can change the volume storage potential [8]. Summarizing, to have an efficient and long-term capture of CO2, the basin needs a large storage capacity and a caprock with very low permeability to avoid possible CO2 losses towards atmosphere.

A process similar to those previously described is the use of CO2 to enhanced oil and gas recovery. This technology, denominated

EOR, allows to use CO2 captured to increase production capacity from oil and gas reservoirs, in fact, around the world the recovery factor of oilfields is about 40% [8]. Among different techniques used for EOR, the gas injection is the one used the most. In our case, the gas injected is the CO2 and It allows to reduce interfacial tension between oil and water causing an easier displacement of oil and, at the same time, It maintains stable reservoir pressure. In the future, more and more power plant with carbon capture will be built and so more CO2 to EOR will be available at lower cost than other gases such as liquified natural gas. For these reasons, EOR can represent an economical option to saline aquifers. Mohammed D. Aminu et al. report that the use of EOR in United States has increased the daily oil production of 250,000 barrels.

A very effective storage option occurs with the use of exhaust oil and gas reservoirs. This storage technology shows a series of advantage [8]:

- before and during the extraction period a very intensive study on the reservoirs was conducted and so we know the storage capacity;
- The entire infrastructure is already there and with or without small modification It can be used to inject CO2 underground with a very important economic advantage rather than other options;
- CO2 injection has been already studied thanks to oil extraction experience;
- the capacity of caprock to confine for very long period CO2 injected without losses is indirectly demonstrate

with the containment of oil and gas for geological period. In fact, on the contrary case, hydrocarbons were not just present;

Another option to store anthropogenic CO2 occurs in unminable coal seams. Coal is characterized by large number of pores which can store considerable amount of gases. CO2 adsorbing is caused by higher affinity with the coal than methane previously adsorbed. In this way, CO2 replaces the methane and can be permanently stored, while methane producing is favoured [8]. Thanks to this option, considerable amount of CO2 can be stored. Enhanced coal bed methane (ECBM) occurs in two demonstration plants: the Alberta Carbon Trunk Line (ACTL) and the San Juan Basin project (USA) [8]. Respect with EOR technology, ECBM is still in research phase and It must be studied better.



Figure 6: Different options of CO2 storage [8]

Other suggested sequestration options can be ocean storage and mineral carbonation. Almost 70% of the earth is covered by oceans with an average depth of 3,800 [m]. Studies have demonstrated that at a depth of 4-5 [km], water moves very slow and if CO2 is injected at these depths, It can remain isolated from atmosphere for very long period [8]. The most important parameters which can be used to evaluate the ocean storage are injection depth, residence time and profile of CO2 concentration [8]. A several studies were conducted to understand the behaviour of CO2 storage in oceans and a series of technical aspects are revealed. CO2 must be injected at a depth major than 1,000 [m] to have a very long sequestration period, but a problem of leakage is also encountered. In fact, over a 50 years injection periods, about 10% of CO2 was released into atmosphere [8]. There are some critical aspects relative to CO2 storage in oceans that can be summarized in [8]:

- possibility of seawater acidification in the proximity of injection point;
- possible negative impacts on organisms;

Another problem related to this option is the classification of CO2 waste. In fact, if CO2 is recognized such as industrial waste, its storage in oceans will be prohibited. All these uncertainties could require a series of specification to regulate this technology.

About mineral carbonation, CO2 captured can be storage throw the reaction with alkaline earth metal oxides or hydroxides [8]. Following reactions are examples of mineralisation tanks to Calcium and magnesium rich mineral [8]:

$$CaO_{(s)} + CO_2 \rightarrow CaCO_{3(s)} \tag{1}$$

$$MgO_{(s)} + CO_2 \rightarrow MgCO_{3(s)}$$
 (2)

We can classify two options:

- in-situ carbonation: CO2 is injected in geological formation to produce carbonate;
- ex-situ carbonation: with the use of local rock, CO2 is used to carbonization directly in the industrial plant above the ground;

### 2.2 Pre-reforming of natural gas

In modern syngas production plant, a pre-reforming section occurs to convert all higher hydrocarbons thanks to following reactions [9]:

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{1}{2}m\right)H_2 \Delta h_{298K}^0 = -1108 \left[\frac{kJ}{mol}\right]$$
(3)

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \ \Delta h_{298K}^0 = 206.2 \left[\frac{kJ}{mol}\right]$$
 (4)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \Delta h_{298K}^0 = 41.2 \left[\frac{kJ}{mol}\right]$$
 (5)

In this way, all higher hydrocarbons (n>1) are converted in an irreversible way thanks to catalyst in the pre-reformer. Exothermic methanation and WGS reactions also occur. The choice of steam-to-carbon ratio and thermodynamic parameters, such as pressure and temperature, are dictated by

inlet fuel. In case of natural gas feed, typical operating conditions are: H2O/C molar ratio of 0.3-2.0 and a range of inlet temperatures between 350-550 [°C] [9]. Concerning to catalyst, high surface area and resistance to poisoning have fundamental importance. Usually, pre-reformed catalyst contains Nickel and the catalyst support are based on alkaline properties to have more carbon formation resistance due to high H2O adsorption over the surface [9]. The carbon formation can be caused by the following general reaction [10]:

$$C_n H_m \to nC + \frac{m}{2} H_2$$
 (6)

There are two options to have carbon formation over eth catalyst:

- Formation of whiskers carbon;
- Polymerization of higher hydrocarbons (gum type);

With low steam-to-carbon ratios, whiskers carbon formation is the main route for carbon formation. In particular, this type of carbon is formed above a certain temperature [9]. On the contrary, gum type carbon formation occurs below a certain temperature. So, we need to operate in a certain range of temperature.

To understand better the limit of carbon formation during prereforming step, a very useful figure is reported in [9]. In this way, we can choose appropriate inlet temperature and H2O/C molar ratio avoiding catalyst deactivation. Summarizing, all higher hydrocarbons can be converted in a mixture of methane, hydrogen and carbon monoxide and carbon formation in the reformer is totally avoided. In this way, possibility to pre-heat gas entering in the reformer over 650 [°C] is possible causing an increase in syngas production capacity with a lower demand of oxygen to partial oxidation, because less heat is required in the reformer.

### 2.3 Natural gas reforming technologies overview

Mature reforming technologies are steam reforming, autothermal reforming and partial oxidation. Today, steam methane reforming is the most used at industrial level. Its production is about a half of total hydrogen produced. Natural gas and water vapour react to produce syngas thanks to a highly endothermic reaction [5]:

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \quad \Delta h = 206 \left[\frac{kJ}{mol}\right]$$
 (7)

Reaction occurs in the temperature range between 500 and 900 [°C], pressure range between 20 and 35 [bar] and steam to carbon ratio major than 2.5 [5]. Without CO2 removal, SMR causes an emission of 9.5 [kgCO2/kgH2] [4]. Large-scale steam reforming plants produce hydrogen at a flowrate between 20,000 and 250,000 [S $m^3$ /h] [11] with high conversion efficiency from 74% to 85% [12]. In case of installing a carbon dioxide

removal section, a reduction of conversion efficiency occurs and, more in detail, [11] estimates an efficiency loss of about 5%. To supply endothermic reaction inside reforming reactor, heat at high temperature is produced by combustion of a part of natural gas in the furnace [12]. In the exhaust gases from furnace, CO2 contained has a low partial pressure that making less efficient a CO2 removal [12]. For this reason, a part of flue gases is vented off directly into atmosphere and the overall reduction of CO2 emissions is around 70% [11].

Partial oxidation is another option to produce syngas. POX is a partial combustion of hydrocarbon with pure oxygen or air flux. It's an exothermic reaction which occurs at elevated temperature around 1500 [°C] and pressure range between 25 and 80 [bar] [5]:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + H_2 \tag{8}$$

A promising solution is to combine partial oxidation and steam reforming. This technology is named autothermal reforming. The idea is to take advantage of heat released by POX to produce syngas from steam reforming of natural gas thanks to nickel catalyst assistance in a one reactor only. Process requires methane, water vapour and pure oxygen or air as feed and following overall reaction takes place [5]:

$$CH_4 + \frac{1}{2}H_2O + \frac{1}{4}O_2 \iff CO + \frac{5}{2}H_2 \qquad \Delta h_{rx} = 84 \left[\frac{kJ}{mol}\right] \qquad (9)$$

Temperature range is in the order of 900/1150 [°C] and large pressure range between 1 and 80 [bar] [5]. Oxygen production causes elevated cost, but the absence of nitrogen in the syngas favours syngas treatment with CO2 removal becoming easier and efficient [13]. Modify oxygen and water vapour at inlet reactor, syngas composition can be changed. In case of autothermal reforming, oxygen can be feed with high purity or through an air flux. In case of pure oxygen, a section of air separation will be installed. Commercial mature technology is cryogenic separation that It is composed by fractional distillation of air at low temperature [14]. Today, this type of plant operates with oxygen production rate major than 150 [t/d] and purity of 99.5% [15]. Also in this case, membranes can be used to separate oxygen from air. As reported by F. Wu et al. [15], membranes can represent an easier and economical alternative rather than cryogenic separation. In case of lower oxygen production rate, adsorption process constitutes a promising alternative [15].



Figure 7: ATR-reformer view [10]

### 2.4 Water-gas shift process

After reforming process, syngas exiting from reformer is principally composed by hydrogen and carbon monoxide. Methane unreacted and water vapour in excess represent are also present in the syngas together other impurities such as argon or nitrogen traces remained after air separation processing. Water gas shift step is necessary to convert carbon monoxide into hydrogen and carbon dioxide with water vapour auxiliaries. The reaction is composed by [16]:

$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta h_{rx} = -41.1 \left| \frac{kJ}{mol} \right|$$
 (10)

Basically, WGS uses oxygen atom contained into water molecule to oxidize carbon monoxide in carbon dioxide with the production of more hydrogen. Generally, reaction is composed by two steps at different temperature to achieve high CO conversion in the range of pressure between 25 and 35 [bar] [17]. Research on catalyst materials is very intensive and, as investigated by Levalley et al., more and more catalyst combinations are available. High temperature shift operates in temperature range of 310/450 [°C] and pressures between 25 and 35 [bar] [17], while low temperature shift is conducted between 210 and 240 [°C] [17]. Generally, iron/chromium and copper/zinc-based catalysts are used in HTS and LTS respectively [17].

	Catalyst material	т [°С]	C/H2O	conv (%)	P [bar]
HTS	Cr/Fe	400	0.125	97	25
LTS	Cu/Zn/Al	200	0.125	>99	25
source	[17]	[17]	[18]	[17]	[17]

Table 3: Optimum values for proven WGS processes

### 2.5 Hydrogen separation process

The most preferred option to separate hydrogen is represented by pressure swing adsorption (PSA), because It allows to recover hydrogen with higher efficiency at high level of purity [6]. PSA system is based on binding forces between crossing gas molecules and adsorbent material [6]. More in detail, adsorption process occurs during the pressurization step, while, on the contrary, the release of adsorbent gases occurs during depressurization step [6]. High pressure step is carried out in the pressure range of 10-40 [bar], while the delivery of depleted gases occurs at low pressures [6]. Concerning on Hydrogen molecule, his high volatility makes hydrogen impossible to adsorb [6]. On the contrary, other molecules composing the stream, such as CO, H2O, hydrocarbons and CO2, are easily adsorbed over adsorbent bed and, in this way, hydrogen separation at high purity occurs [6]. PSA system allows to obtain hydrogen recovery in the range of 70-90% with a very high purity range of 98-99.999% [6].
# 2.6 Advanced natural gas reforming technologies

New promising alternatives to produce Hydrogen are based on the idea of coupling reaction and separation steps. In fact, hydrogen is produced thanks to equilibrium-limited reactions and if H2 or CO2 is removed the conversion factor increases [5]. To give a general description, we can follow two different options [5]:

- High purity hydrogen could be obtained coupling the process of WGS with membrane to remove H2 (WGS-MR) or to use a reformer membrane reactor where reforming, WGS and membrane separation occur (SMR-MR);
- To achieve CO2 purity requires to transport, the technology of sorption-enhanced WGS or sorptionenhanced reformer is needed to reach the scope;



Figure 8: Schematic summary of advanced technologies to produce hydrogen [5]

The WGS-MR research technology is just at lab scale. The process operates in the range of temperature between 300 and 500 [°C] and, in this range, dense metallic and ceramic membranes can operate [5]. About SMR-MR, ceramic membranes can be used in reformer, because they can operate at high temperature between 600 and 900 [°C] [5]. An important pilot plant has been constructed by "Tokyo gas" in cooperation with "Mitsubishi Heavy Industries" to simulate a membrane reformer [5]. More in detail, the plant has been developed to produce 40 [ $Nm^3/h$ ] of hydrogen with purity higher than 99.999% and an efficiency of 70-76%, based on HHV [5]. A pd-alloy membrane is used into reformer and only at the end of testing period, impurities concentration appeared, but the H2 purity is always higher than 99.99% [5].

The sorption-enhanced technology is based on the continuously removal of a specific product to enhance conversion efficiency. In SE-WGS, CO2 is removed during the process of WGS causing an amount of hydrogen produced [5]. Moreover, SE-WGS technology is only employed at pilot scale. Similar to SE-WGS is the SE-SMR technology, but the reactions take place at higher temperatures [5]. The optimal reactor is a circulating fluidized bed typology respect with fixed-bed one, because high temperature occurs [5]. Heat useful to the reaction can be produced from fuel combustion in the regenerator or supplied by an external heat source [5].

Recently, syngas chemical looping technology has received more and more attention. Processes is composed by three reactors: fuel reactor, steam reactor and air reactor [5]. Syngas oxidizes into fuel reactor thanks to an oxygen carrier based on iron oxide. After that, the reduced iron oxide is supplied to steam reactor, where It is recycled by oxygen contained in a feeder stream composed by steam, while hydrogen separation occurs [5]. Complete regeneration of oxygen carrier is obtained into air reactor and, after that, another cycle can be initialized [5]. Syngas produced from natural gas decomposition contained few impurities and so hydrogen and carbon dioxide produced by chemical looping have a purity level to be transport [5].



Figure 9: Chemical looping cycle [5]

# 3 Methodology and Assumptions

After a general description on state of the art of hydrogen production and carbon capture, there is the necessity to define in a detailed way the plant, before to start the techno-economic study. So, in the following lines, a series of choices will be introduced:

- Choice of plant technology;
- Research of a strategic area to install the plant;
- Plant description;
- Technical assumptions;
- Economic assumptions;

# 3.1 The choice of plant technology

This thesis analyses a hydrogen production plant from natural gas reforming coupling with carbon capture and It will be leaded to mature technologies. As mentioned above, there are a lot of promising reforming technologies such as chemical looping and sorption-enhanced process, but substantially there are only two commercial mature reforming ones: steam methane reforming (SMR) and autothermal reforming (ATR).

When a carbon capture unit is added, natural gas consumption of the power plant is higher. In case of SMR the increment of natural gas consumption is 39% respect with 5% of ATR causing an amount of energetic cost [13]. This increment of natural gas consumed, in case of ATR, causes a higher oxygen demand and consequently the cost of air separation unit (ASU). The necessity of an ASU in ATR option could be causing both technical and economic penalty.

Pay attention to carbon capture scope, ATR allows to have major CO2 removal respect with SMR. In SMR case there are two streams containing CO2: one exits from furnace and the other exits from reforming section. Flue gas exiting from furnace has low CO2 partial pressure which, in case of CO2 removal section, causes very low removal efficiency [7]. The highest CO2 partial pressure is found at the exit from reforming section where a capture process can be efficiently installed [7]. So, in case of SMR, around 85% of CO2 is captured by syngas, while the other 15% together with flue gases exiting from furnace are vented to atmosphere and an overall CO2 capture of 70% is reached [11]. In the ATR, a more efficient CO2 removal is achieved, because CO2 is entirely concentrated in a stream. Thus, possible CO2 losses could derive from PSA off tail gases, which can be combusted to provide heat and electricity to plant integration.

Another advantage related to ATR is the simpler reformer design than fired tubular reformer, which represents the actual design to SMR plants. For this reason, ATR presents a lower investment cost of 15-25% than SMR reformer [19].

Summarizing, after this technical comparison between reforming options, the choice falls on ATR plant, because some positive aspects can be used, which are:

- Lower reformer reactor cost;
- Possibility to have higher CO2 removal rate;
- Lower losses in thermal efficiency;

• Contained amounts on natural gas consumption when a CCS is installed;

## 3.2 Assessment of a possible location of the plant

Concerning on choice of plant location, Algeria, in the North Africa region, can be a promising option. In fact, It presents important hydrocarbons resources other than a huge amount of solar and wind energy to produce hydrogen via water electrolysis in the long term period [20]. Nowadays, hydrocarbons, in particular way natural gas, can be used to produce hydrogen thanks to thermal decomposition processes like autothermal reforming as in our case [20]. The presence of a consolidated sequestration and storage site in In Salah region is very important to permanently capture CO2 and an existing pipeline network linked to European Union allows to transport the hydrogen produced. Recently, a higher amount of local consumption caused by population increment could represent an advantage to future potential investments of external companies, because Algeria should satisfy a major demand of energy [20]. In particular, Hydrogen is easy to transport and It can be stored for long period with few losses, so It could represent an efficient strategy to Algeria to satisfy higher internal energy demand [20]. According to Oil and Gas, as reported in [20], Algeria is in the seventh position of world natural gas ranking with an amount of 4.6 trillion  $[m^3]$  of gas resources, but the recoverable ones are much higher. Hassi R'Mel is the biggest natural gas hub of the country. It is situated in the centre of the region and It represents more than half of

the entire certificated reserves [20]. Other sites are positioned in the South regions, such as In Salah, and in South-east regions such as Rhourde Nouss and In Amenas. Algeria is equipped by an important pipeline infrastructure to transport natural gas both to export and internal domestic needs. Hassi R'Mel represents the central point for all pipelines. The most important natural gas fields are linked to Hassi R'Mel thanks to a 1,650 [km] pipeline length [20]. About to internal natural gas use, a 1,550 [km] gas pipeline links Hassi R'Mel to Meditteranean cost, where the biggest part of the population lives [20]. Concerning to European export, two major pipelines were built in the past: one links Algeria to Italy starting from Hassi R'Mel via Tunisia and Meditteranean Sea with a length of 1,100 [km] and the other one links Algeria to Spain via Marocco with a 1,600 [km] line [20]. The connection between Algeria and Italy is named TRANSMED "Trans Mediterranean Pipeline", known as "Enrico Mattei" gas pipeline. Following a stipulation of natural gas contract for 25 years, TRANSMED was built between 1978-1983 years with a capacity of 12.3 billion cubic meters per year. Recently, as mentioned by "Sole 24 Ore" journal, "Eni" and "Sonatrach", hydrocarbon state companies of Italy and Algeria respectively, have updated natural gas export contract until 2027 with a total capacity of around 10  $[Gm^3]$ . So, there is an important presence of "Eni" in the country with an intensive collaboration with

"Sonatrach".



Figure 10: The figure helps to understand the exact disposition of natural gas field and pipeline in Algeria's country (source: <u>http://energy-cg.com/OPEC/Algeria/Algeria\_OilGas\_Industry.html</u>)

As we can see in the figure above, two large natural gas field regions can be individuated: one in the south region and the other one in the south-west regions. Both of them are efficiently linked to most important natural gas centre Hassi R'Mel, where natural gas extracted is partitioned to be transported towards importing countries. More in detail, three principal natural gas projects looking for Timimoun, In salah and In Amenas regions are presented. All dates about Timimoun and In Amenas project were extracted from "Hydrocarbon-Technology" site.

The Timimoun field has recently started to produce gas. It is characterized by a tight gas reservoir. The gas field is situated in the south-west of the region among other fields such as Touat, Ahnet and Reggane North fields. The project is in collaboration with "Sonatrach", "Total" and "Cepsa" ("Compania Espanola de Petroleos"). An area of 2,500  $[km^2]$  is covered by the project with a production of 1.6 billion  $[m^3]$  of natural gas per year.

In the In Amenas region, a large gas project was realized thanks to collaboration between "Sonatrach", "BP" and "Norway's Statoil". It produces around nine billion of  $[m^3]$  of natural gas per day over an area of 2,750  $[km^2]$ . At starting point, 85  $[Gm^3]$  of gas were estimated thanks to four gas fields (Tiguentourine, Hassi Farida, Hassi Ouan Taredert and Hassi Ouan Abecheu). The proximity of the Libia to In Amenas region causes high instability risk. At the beginning of 2013, a terrorist attack, during the installation of a compression plant to maintain a stable production of Gas, occurred and 40 people was killed. For this reason, limited production was maintained until security conditions were restarted.

Focusing on this study, a very important project regards the area of In Salah. In Salah Gas project is started from 2004 thanks to a collaboration between "BP" (33%), "Sonatrach" (35%) and "Statoil" (32%) [21]. During project construction, two phases can be individuated: in the first phase three gas plants, Krechba, Teg and Reg, were developed to achieve a production of 9 [ $\frac{Gm^3}{year}$ ] at 2004, while other four gas plants were developed in the second phase to maintain a stable production when the first phase project production will be decreased. The second phase of project, with the development of other four gas fields, including Garet el Befinat, Hassi Moumene, In Salah and Gour Mohmoud, started in February 2011 and its conclusion was expected for 2014. Moreover, the previously mentioned terrorist attack in In Amenas region, causes a delay of the project. So, the last four gas fields started in February 2016 and an overall production of 14.1  $\left[\frac{Mm^3}{d}\right]$  was achieved. In Salah project interests an area of 25,000  $[km^2]$  with a natural gas potential production of 340  $[Gm^3]$  as stated by "Hydrocarbons-technology" site.

A key point of the project is the presence of a deep underground formation to geological sequestration of CO2. This formation is an exhausted oil and gas reservoir situated at different deep: 1,800, 1,850 and 1,900 [m] respectively [8]. More in detail, natural gas extracted from In Salah region is processed to remove the too high CO2 content and to avoid carbon dioxide emissions into atmosphere. It is re-injected into underground storage [21]. The total storage capacity of 17 [Mt] of CO2 is estimated with an actual injection rate of 4,000 [t/d] [8]. Concerning to economical point of view, the cost of CO2 injection is around 6 [\$/t] and a total storage cost of 2.7 billion of US\$ has been planned [8].

The injection started from 2004 and an intensive monitoring and studying phase was started to understand all critical aspects about CO2 underground injection [21]. These studies are very important, because CO2 sequestration underground will be of fundamental importance in the future to reduce CO2 emissions. On 2011, a stop of injection operation was caused by some suspects on caprock integrity of the site, but any CO2 leakage into atmosphere appeared [21]. Another aspect in researching phase is the possibility that CO2 injection causes seismicity, which could drastically reduce the public acceptance of CO2 sequestration in populated regions [21]. Summarizing, the presence of a several natural gas fields containing an important amount of natural gas and the possibility of in-situ CO2 sequestration represent a potential site to install a reforming plant with CO2 capture maintaining transport and injection costs of the CO2 captured low. In addition, an existing pipeline infrastructure allows to transport the hydrogen produced towards other parts of the country and European Union. In fact, as mentioned in 1, Hydrogen can be put inside natural gas pipelines with a concentration between 5-10% actually. In this way, we can obtain a decarbonisation of the final user of the energy vector and a definitive storage of the CO2 underground. More in detail, Krechba site can be represent an optimal plant position. In fact, there is the presence of injection wells to storage CO2 in the underground reservoir. This site is only 455 [km] far away from Hassi R'mel natural gas Hub and It is in proximity of a natural gas pipeline.

#### 3.3 Plant description

Scope of this study is to evaluate performance and cost of an autothermal reforming plant with carbon dioxide capture which produces, at the battery limit, Hydrogen and carbon dioxide flow. A scheme of the plant is reported in the figure below, where the main sections of the plant are illustrated.

Reforming section is composed by a pre-reformer unit followed by an autothermal reformer. Syngas exiting from the first part of the plant is shifted in a WGS section to convert CO in more H2 and CO2. After that, carbon dioxide capture section, based on amine scrubbing, removes CO2 from syngas, before the hydrogen purification section based on PSA. PSA-off gases are used to produce steam and electricity to employ in the processes. CO2 captured will be compressed to 110 bar before to be delivered in a pipeline to be transported on injection site. This brief general plant description will be followed by a detailed description of every component.



Figure 11: General scheme of the plant with main inputs and outputs

#### 3.3.1 Air separation unit

The reaction of partial oxidation in the first section of ATR combustor needed a pure oxygen flux. To do that, the plant requires a section where a flux of air is fractionated to produce oxygen. More in detail, ASU installed in this plant is based on cryogenic separation, because It's a tested technology at industrial level.

External air, at ambient pressure and temperature, enters in the ASU at a certain rate. Oxygen produced at the outlet of the section is in low pressure state and a line of compression will occur. After the compression, pre-cooling and purification of inlet air, oxygen is separated in a cold box composed by multiple columns at different pressure level. The process consumes any external fuel, but only electricity. As reported in [22], the electricity consumption of ASU is 0.38 [ $\frac{kWh}{Nm^3}$ ] of low pressure oxygen separated. After that, a line of compression is necessary to feed high pressure oxygen to ATR reformer.

## 3.3.2 Pre-reformer and autothermal reformer section

This section is fundamental to produce syngas, a mixture of hydrogen and carbon monoxide principally. Natural gas entering the plant is get directly from natural gas pipeline. It is at a pressure of 70 [bar] with a temperature of 50 [°C] and to achieve an initial pressure of 25 [bar] an expansion is necessary. The choice to take inlet pressure at 25 [bar] is mainly due to two

problems. As citated in [23], hydrogen produced, during reforming reaction, decreases when pressure increases. So, a pressure as low as possible should be taken. The second problem is related to the presence of a WGS section to carbon monoxide conversion. In fact, as reported in 2.4, WGS operates in a range of 25-35 [bar]. So, pressure of 25 [bar] is set to cover pressure losses in every component and to have a pressure slightly lower than 25 [bar] at the WGS inlet.

After the expansion, methane is mixed with a water vapour flow, at 25 [bar] and 350 [°C], to achieve a ratio of 0.25  $\left[\frac{mol_{H_2O}}{mol_C}\right]$  [9]. After that, before entering in the pre-reformer, mixed flow is heated up to 400 [°C] [9]. At this temperature and steam to carbon ratio any carbon formation occurs on the Nickel catalyst bed inside the pre-reformer [9]. Exiting from pre-reformer, syngas flow is mixed with a water vapour to reach a ratio of 1.5  $\left[\frac{mol_{H_2O}}{mol_C}\right]$  and, before feeder the ATR, It is heated up to 650 [°C] to rich a reformer temperature in the range of 900-1150 [°C] [5]. At the inlet of ATR reactor, oxygen is added to have partial oxidation of natural gas, which produces heat to catalytic reforming. An Oxygen to methane ratio of 0.6 is set [10]. Hot syngas, leaving ATR reformer, are cooled down to an appropriate temperature of 320 [°C] to WGS process.

Value	PRE-REFORMER	ATR REACTOR
Inlet Temperature [°C]	400	650
Pressure [Bar]	24.25	23.5
H20/NG	0.25	1.5
O2/NG	-	0.6

Table 4: Main input values to pre-reformer and ATR reformer

#### 3.3.3 Water gas shifting section

In the WGS, an almost total conversion of CO into hydrogen and carbon dioxide is achieved thanks to an important amount of water vapour added before entering the HT-WGS. Oxygen carried by water vapour is useful to oxidize CO into CO2. A steam to CO ratio of 4.0 is set in the simulation [18]. In the first step, syngas enters the HT-WGS at a temperature of 320 [°C] [17]. Reactions are slightly exothermic and so a higher temperature at the outlet is achieved. A syngas cooler is needed to set a temperature of 200 [°C] at the inlet of LT-WGS [17]. Converted syngas exiting from WGS section is cooled to a low temperature of 40 [°C] and, before entering the capture section, in a separator a water recovery occurs.

Value	HT-WGS	LT-WGS
Temperature [°C]	320	200
Pressure [Bar]	22.75	22.25
H20/CO	4.0	-

Table 5: Input values to WGS section

#### 3.3.4 Carbon dioxide capture section

Concerning to Carbon capture section of the plant, as reported in [24], a CO2 recovery from syngas flow equals to 90% is set, because this value minimized the thermal energy penalty. As also mentioned in the "IEAGHG document" [25], in the recent years the percentage of CO2 capture is set starting from 90%, because there are more severe targets about the greenhouse emissions.

The system selected to remove CO2 from flue gases exiting from WGS process is based on amine scrubbing. It is composed by an absorber and stripper column principally. Shifted syngas from WGS section is cool down at 40 [°C] before entering in absorber [26]. Inside absorber, syngas move counter currently with the chemical absorbent and CO2 contained in the syngas reacts chemically with the solvent [24]. At the top of the absorber column, CO2 depleted flue gases enters in a scrubber to recover water and solvent. Otherwise, at the bottom, rich solvent of bounded CO2 moves towards stripper column, where solvent will be regenerated and a CO2 pure stream will be obtained [24]. During amine regeneration inside stripper, reboiler temperature in the range of 100-140 [°C] is required causing a huge consumption of heat [27]. Concerning on absorber column, values around atmospheric pressure occur, while in the stripper one values around 2 [bar] are imposed [24]. The chemical solvent used is based on amine and more in detail monoethanolamine (MEA), because It has good technical and economical properties to be employed at industrial level.

Some parameters should be changed to achieve an optimal configuration of the absorption process. We can individuate as main parameters the following ones [24]:

- CO2 lean solvent loading  $\left[\frac{mol_{CO_2}}{mol_{MEA}}\right]$ ;
- Amount of CO2 removed;
- MEA concentration in the solvent;
- stripper pressure;
- temperature of the lean solvent at the inlet;

To have an overview on the operating and capital costs of the process, these parameters are varied to find optimum values of:

- thermal energy to solvent regeneration in the stripper [GJ/ton CO2];
- cooling water required  $\left[\frac{m^3}{t_{CO_2}}\right]$ ;
- rate of the solvent  $\left[\frac{m^3}{t_{CO_2}}\right]$ ;

Mohammad R.M. Abu-Zahra et al. [24] have conducted an optimization study in case of 90% of CO2 removal of these parameters. The most important indicator is the thermal energy required by the amine regeneration in the stripper column, because It causes an important energy penalty.

Concerning to MEA concentration in the solvent, corrosion and degradation problems related to the type of chemical solvent limit concentration about to 40%, but at industrial level 30% of MEA concentration is used [24]. Lean solvent loading value determines how much stripper regeneration should be high. In particular, low values mean high thermal energy require,

because more heat is required. An optimum value of 0.32  $\left[\frac{mol_{CO_2}}{mol_{MEA}}\right]$  is founded [24]. Stripper pressure has to be as high as possible, because It represents the main driving force of the CO2 mass rate along the stripper column. Increasing pressure, a decrement of the thermal energy required occurs [24]. In the study, maximum pressure investigated is used in the stripper with a value of 2.1 [bar] [24]. Effects on thermal energy required are also due to lean solvent temperature at absorber inlet. More in detail, low solvent temperature around 25 [°C] has minimum thermal energy expenses, but this value can be difficult to achieve. So, optimum value corresponds to lowest solvent temperature achievable [24]. In fact, in a simulation of MEA scrubbing reported in [27], a more real temperature value of 40 [°C] is used. In the following table, from [24], a list of the major parameters useful to model the CO2 removal system are used as reference.

Reference parameters	MEA (30%)
CO2 removal [%]	90
lean solvent $\left[\frac{mol_{CO_2}}{mol_{MEA}}\right]$	0.32
rich solvent $\left[\frac{mol_{CO_2}}{mol_{MEA}}\right]$	0.493
lean solvent temperature [°C]	25
solvent flow rate $\left[\frac{m^3}{t_{CO_2}}\right]$	27.8
stripper pressure [bar]	2.1
heat required $\left[\frac{GJ}{t_{CO_2}}\right]$	3.29

Table 6: Reference parameters to simulation of CO2 process



# 3.3.5 Hydrogen purification section

For hydrogen purification, pressure swing adsorption section occurs after CO2 removal section. PSA is the most used process to separate hydrogen at high purity with high percentage of recovery, as described in 2.5. In this study, PSA is designed to achieve a high recovery of hydrogen, because It will represent the product of the plant. So, a recovery of 90% is set. As citated in [6], PSA will be composed by a minimum of four adsorbent beds to allow a continuative hydrogen production. The process will be conducted at ambient temperature. At the end of the process, two principal streams will be obtained: one is composed by high purity hydrogen recovered and the other one is composed by exhaust gas at a lower pressure. Inlet pressure and temperature of the syngas entering the PSA section are reported in Table 7, as suggested by Voldsund M. et al. [5].

Value	PSA
H2 capture [%]	90
H2 purity [%]	>99
Inlet Temperature [°C]	25
Inlet Pressure [bar]	21

Table 7: Performance parameters to PSA simulation

# 3.3.6 Exhaust gas recovery section

Residual gases exiting from PSA section contain, other than a lower percentage of methane unconverted, 10% of overall H2 produced after WGS section mixed with other residual of CO, CO2 and water traces. These gases have a good heating value and their combustion is necessary. In this way, more heat available to plant integration will be produced. Moreover, this configuration will cause an amount of CO2 emission, because after combustion all gases are vented into the atmosphere. To model the combustor, a flow of combustion air will be calculated to limit a combustion chamber temperature of around 900 [°C] to avoid material degradation.

## 3.4 Technical assumptions

After a detailed description of every section present into the plant, it is important to define the main input/output of the plant. Other than produce hydrogen, the plant has the objective to capture carbon dioxide in order to decarbonize energy vector. The size of the plant is selected fixing hydrogen flow rate at the exit of the plant limit and the input of natural gas is found.

## 3.4.1 Plant capacity

Based on the hydrogen rate produced at the outlet of the plants, we can classify them in small, medium and large ones. Generally, small and medium plants are characterized by a hydrogen production rate up to 20,000  $\left[\frac{Sm^3}{h}\right]$ . In case of large plants, more than 100,000  $\left[\frac{Sm^3}{h}\right]$  of hydrogen rate is produced [11]. Concerning to single cost and complexity of the reformer, ATR presents some advantages respect with SMR, but the air separation unit represents a very high cost which is up to 40% of the overall synthesis gas plant cost [28]. For this reason, a possibility is represented by use of air instead pure oxygen, but a huge amount of nitrogen in the flue gas had to be take in consideration and this causes bigger gas volumes to process like, for example, PSA. In case of carbon capture option, the presence of nitrogen causes elevated energy cost to separate CO2. So, in our case, an air separation unit is to be employed to have an efficient hydrogen production with carbon capture. To split the huge cost of ASU, a large size of the plant will be chosen to investigate the possibility to produce hydrogen at competitive cost while CO2 capture occurs. In particular, the plant will be designed to produce 100,000  $\left[\frac{Nm^3}{h}\right]$  of hydrogen.

## 3.4.2 Plant location

Krechba site is selected as a potential plant position thanks to:

- Presence of a natural gas pipeline where natural gas can be easily extracted;
- Presence of an operating infrastructure to sequestrate carbon dioxide in an underground storage directly in the proximity of the site;

LOCATION	
State	Algeria
Plant Site	Krechba
Site Condition	Desertic zone
AMBIENT CONDITIONS	https://www.climieviaggi.it/clima/algeria
Average Temperature [°C]	25
Max Temperature	45
Min Temperature [°C]	6
Ambient Pressure [bar]	1.013

Table 8: List of main assumptions related to plant location

The investigation assumed that all external infrastructure such as, water, electricity grid, civil works, transport infrastructure useful to plant functioning are already present and available.

# 3.4.3 Capacity factor

During first year of operation, a capacity factor of 70% is assumed, while a plant availability of 95% is assumed for the rest of the plant life [29].

#### 3.4.4 Input Specifications

Standard natural gas is the input fuel for our plant. In the technical analysis, the composition chose is proper to Algeria's natural gas and It is reported in the table below. At the plant limit, natural gas is assumed at 70 [bar] and 15 [°C] [30].

NATURAL GAS ANALYSIS [VOL%]	[27], [28]
Methane	87.92
Ethane	6.95
Propane	0.59
Butane	0.59
Pentane	0.59
CO2	0.97
N2	2.29
pressure [bar]	70
HHV[MJ/Smc]	40.09
LHV[MJ/Smc]	36.23

Table 9: Natural gas composition of Algeria used in the simulation

Process water is employed to natural gas reforming and WGS process. For this reason, water flow is composed by demi-water to avoid catalyst degradation and to improve processes. To account this requisite, in the economic assumptions, a major cost is provided.

About to cooling system, raw water is used. Inlet and outlet cooling water temperature are set to 15 [°C] and 30 [°C] respectively. Knowing the temperature difference, the flow rate required by the cooling system can be calculated.

Ambient air is fed to ASU and tail gas combustor at ambient pressure and temperature define in the Table 8. The molar composition assumed is composed by 79% of N2 and 21% of O2. In the Aspen simulation, a purity of 100% of oxygen produced have been assumed.

## 3.4.5 Product specifications

Products of the selected plant are hydrogen and carbon dioxide captured. Hydrogen is produced at 70 [bar] and 40 [°C]. As for oxygen produced, in the aspen simulation the purity of hydrogen exiting from separator is assumed at 100%. Carbon dioxide captured exits the plant at 110 [bar] and 30 [°C] with a purity higher than 98%. This high purity allows to inject CO2 in the underground storage site.

As mentioned during introduction, hydrogen can be mixed with natural gas inside pipelines until to reach a concentration of 10% wt. In Salah pipeline has a natural gas flowrate of around 14  $\left[\frac{Gm^3}{d}\right]$  and so we could inject 1.4  $\left[\frac{Gm^3}{d}\right]$  of hydrogen, which will correspond to a production of 58,000  $\left[\frac{Nm^3}{h}\right]$ . Andrzej Witkowski et al. [31] have conducted a study in which different hydrogenmethane mixture concentration are investigated. In the range of 5-15% only minor problems can be occurred [31]. Concerning this study, if all hydrogen produced is putted in the pipeline, a mixture of hydrogen and natural gas major than limits mentioned will occur and a series of technical problems could be caused. So, an alternative method to deliver the hydrogen produced should be investigated, but It is out of our scope.

#### 3.5 Model simulation

The hydrogen production plant is modelled with Aspen HYSYS version 8.8. It is a chemical process software specialized in

hydrocarbon steady state processes. In the simulation, Peng-Robinson is the set of equation used in the reforming section, while in the simulation of carbon dioxide capture process an Acid Gas package is used.

## 3.6 Performance indexes

The plant considered converts chemical energy contained in natural gas into hydrogen, steam and electricity and It captures the major part of CO2 produced, releasing the remaining one. To have an appropriate comparison respect with other plant, a series of indices will be necessary to define. As reported by Martinez I. et al. [32], performance parameters, which will be introduced, are:

• Equivalent natural gas flow rate:

$$\dot{m}_{ng,eq} = \dot{m}_{ng} - \frac{\dot{Q}_{th}}{\eta_{th,ref} * LHV_{NG}} - \frac{W_{el}}{\eta_{el,ref} * LHV_{NG}}$$
(11)

• Hydrogen production efficiency:

$$\eta_{H_2} = \frac{\dot{m}_{H_2} * LHV_{H_2}}{\dot{m}_{ng} * LHV_{NG}}$$

(12)

• Equivalent hydrogen production:

$$\eta_{H_{2},eq} = \frac{m_{H_{2}}*LHV_{H_{2}}}{m_{ng,eq}*LHV_{NG}}$$
(13)

• Carbon capture ratio:

$$CCR = \frac{\dot{m}_{CO_2,capt}}{\dot{m}_{ng}*LHV_{NG}*E_{NG}}$$
(14)

• Equivalent carbon capture ratio:

$$CCR_{eq} = \frac{\dot{m}_{CO_2,capt}}{\dot{m}_{ng}*LHV_{NG}*E_{NG}-\dot{Q}_{th}*E_{th,ref}-W_{el}*E_{el,ref}}$$
(15)

• CO2 specific emission:

$$E_{CO_2} = \frac{\dot{m}_{CO_2,vent}}{\dot{m}_{H_2} * LHV_{H_2}} \left[\frac{gCO_2}{M_{Ith}}\right]$$
(16)

• Equivalent CO2 emission:

$$E_{CO_{2},eq} = \frac{m_{CO_{2},vent} - Q_{th} * E_{th,ref} - W_{el} * E_{el,ref}}{m_{H_{2}} * LHV_{H_{2}}} \left[\frac{gCO_{2}}{M_{J_{th}}}\right]$$
(17)

The most general index is related to hydrogen efficiency which quantifies the overall efficiency of the plant to produce hydrogen from natural gas. The introduction of an equivalent natural gas flow rate has the purpose to take into account, other than H2 produced, steam and electricity produced/demanded by the plant, which will be evaluated with specific industrial parameters. In particular,  $\eta_{th,ref}$  and  $\eta_{el,ref}$  with values of 0.9 and 0.583 respectively [32], are general efficiency values obtained in natural gas and boiler industry. As for hydrogen efficiency, an equivalent hydrogen production efficiency is introduced thanks to equivalent natural gas flowrate. The plant captures carbon dioxide thanks to an amine section and so, indexes related to carbon capture ratio are presented to evaluate CO2 capture efficiency. Carbon capture ratio (CCR) is the ratio between CO2 capture flow rate and the CO2 mass flow rate related to natural gas entering the plant. Specific emission  $(E_{NG} = 57 \left[\frac{gCO_2}{M_{LHV}}\right])$  is chose by Martínez I. et al. [32]. An equivalent CCR is also introduced. As for hydrogen production and CCR ratio, also for CO2 emissions the technical analysis is based on equivalent and traditional emission indexes. In the specific emission, only natural gas flow rate is considered with his emission factor  $(E_{NG})$ , which quantifies how much CO2 per  $[MJ_{th}]$  is emitted. Concerning to equivalent emission, also emissions from thermal and electricity production/demand are accounted throw specific emission parameters, which are:  $E_{th,ref} = 63.3 \left[\frac{gCO_2}{MI_{th}}\right]$  and  $E_{el,ref} = 97.7 \left[\frac{gCO_2}{MI_{th}}\right]$  [30]. In case of electricity production taking advantage from available heat, a conversion factor of 0.25  $\left[\frac{MJ_{th}}{MI_{el}}\right]$  is assumed in this study [32].

# 3.7 Reference plant

To perform a better techno-economic comparison on results obtained, a reference plant is chosen. The choice of reference plant is based on SMR reforming, because It represents the state of the art of hydrogen production. Reference plant is designed to produce the same hydrogen output of ATR plant. All technical and economic assumptions done in the previously paragraphs remain valid. The plant is composed by the following sections:

- Reforming section;
- Water gas shift section;
- CO2 capture section;
- Hydrogen separation section;

Reforming section is composed by a pre-reformer followed by a SMR reformer. Other than methane, natural gas contains some heavy hydrocarbons and traces of impurities. In the pre-reformer, heavy hydrocarbons are converted thanks to equations reported in 2.2. Before to enter the pre-reformer, natural gas is mixed with steam to achieve a steam to carbon ratio of 4.0 [32] and pre-heated to 400 [°C] as for ATR case. Steam to methane ratio chosen is higher than normal one adopted in plant without carbon capture [32]. In fact, there is the necessity to achieve a higher CO conversion in WGS section in order to have an efficient CO2 removal. As for ATR plant,

converted natural gas is heated up to 600 [°C] before to enter the reformer. Reformer is based on fire tubular reformer (FTR), which represents the state of the art of SMR reformer. The SMR reaction, explained in 2.3, occurs inside tube filled with Nickel catalyst. Here, natural gas mixture is converted in syngas in a temperature of 890 [°C] [32]. Heat needed to reformer reaction is produced in the furnace, where gases remained after hydrogen separation and natural gas burn. Gases exiting from hydrogen separation section present a heating value that allow to consume less natural gas. Syngas produced is cooled down to 320 [°C] before to enter the high temperature shift reactor, where CO is converted in more CO2 and H2 as explained in equation (10). Due to exothermicity of the reaction, syngas should be cooled down to 200 [°C], before to enter the second shift reactor. At the end of the process, only a little unconverted amount of CO remained in the syngas (1.8 [mol%]). CO2 capture section is based on MEA scrubbing and It is made of in the same way of ATR case, described in 3.3.4. Syngas has to be expanded at 1.5 [bar] and cooled down to 40 [°C] before to enter MEA system, which is designed to capture 90% of the total CO2 contained in the syngas. After CO2 de-hydration, CO2 is compressed to 110 [bar] to be transported. The technology chosen to separate hydrogen is based on PSA, because It is widely used in commercial applications. Scrubbed gas exiting from the top of absorber column at low pressure has to be recompressed before to enter into PSA system, because It works at higher pressures, as described in 2.5. Due to high temperature reached during the recompression process, scrubbed gas has to be cooled down to ambient temperature. A separation of 90% of total hydrogen contained is achieved with a purity of 99.99%, as for ATR case. Hydrogen separated will be compressed to 70 [bar] and 25 [°C], before to be delivered. As mentioned above, remain gases exiting from PSA are supplied to furnace to be burned with natural gas and air. All the availability of heat at the end of the process is used to produce steam at high pressure to feed a steam turbine. In this way, there is a production of electricity, which is used to integrate the plant consumptions. A part of the steam exiting the turbine at low pressure is supplied to stripper column to allow amine regeneration.

#### 3.8 Sensitivity Analysis

Sensitivity analysis is important to understand better the possible LCOH variations during operating life of the plant. The most important cost factor is the natural gas cost. As reported in [25], fuel price has to be varied from -50% to +100% of the cost assumed. Concerning on CO2 transport and storage cost, sensitivity range is between 0 and 20  $\left[\frac{\epsilon}{t_{CO_2}}\right]$  [25]. About to electricity cost variation, a range between 40 and 100  $\left[\frac{\epsilon}{MW_h}\right]$  is assumed. The most scope of the plant investigated is to capture CO2. So, a sensitivity ranges adopted are reported in the table below.

Natural gas cost	$\left[\frac{\in}{GJ_{LHV}}\right]$	3 to 6
Elelctricity cost	$\left[\frac{\epsilon}{MW_h}\right]$	40 to 100
CO2 transport and storage cost	$\left[\frac{\epsilon}{t_{CO_2}}\right]$	0 to 20
CO2 emission cost	$[\frac{\epsilon}{t_{CO_2}}]$	0 to 100

Table 10:Range of selected costs to investigate a sensitivity analysis

## 3.9 Economic assumptions

In the next sub-paragraphs, a detailed economic analysis will be presented to be applied in plant economic investigation.

# 3.9.1 Financial structure

After the technical analysis above reported, a cost analysis is fundamental to investigate the plant from an economical point of view. The methodology employed is referred to "NETL-National Energy Technology Laboratory, U.S. Department of Energy-models and reports".

This type of analysis is optimal to evaluate power producing plant costs. Financial structure is based on four levels of capital costs which can be easily summarized in the following figure:



Figure 12: Scheme of general financial structure adopted by NETL

BEC, EPCC, TPC and TOC are classified as "overnight" costs and they are expressed in constant-currency. Constant-currency analysis is referred to "base year" and not accounts effects of inflation so we can have a real cost trend. For example, when we conduce long term studies, such as 20-30 years, constantcurrency analysis can be fundamental to have a real cost trends due to not accounted of many years of inflation.

The sum of capital expenditures gives the TASC. In this case, TASC is reported on current-currency and so taking into account the effect of inflation over capital expenditure period, which corresponds to three years in case of natural gas plant. This analysis requires the use of a discount rate that is equal to the cost of money at the prevailing rate of inflation. In this case, constant-currency analysis of cost is adopted and so the discount rate is represented by the weighted cost of capital in the absence of inflation. Now, a brief description of all parts of financial structure is presented.

Bare Erected Cost (BEC) comprises the cost of process equipment and all infrastructures that support the plant (shops, offices, labs etc) other than direct and indirect labor required for construction and installation.

Engineering, Procurement and Construction Cost (EPCC) comprises the BEC plus costs related to services provided by contractor such as project/construction management costs, contractor permitting and detailed design. Contracting strategy is based on multiple subcontracts, because with this approach the owner can reach a greater control of the project minimizing risk premiums which are included in an EPC contract. In fact, in the market, contractor premiums for these risks can increase the overall project cost dramatically. So, Engineering, procurement and construction management (EPCM) is a most cost-effective approach and these services are estimated at 8-10% of BEC.

Total plant cost (TPC) includes BEC, EPCC and process and project contingencies. Process and project contingencies include those costs which are unknown or unforeseen. Process contingency compensates the uncertainty in cost estimates caused by the development status of a technology. Process contingencies are applied to each plant section based on current technology status, while project contingency is estimated to 15-30% of the sum of BEC, EPC and process contingency.

Total overnight cost (TOC) includes TPC plus all owner's costs, which are the following:

- Pre-production cost takes into account waste disposal, operating labor and maintenance material (2% of TPC);
- Inventory capital estimates at 0.5% of TPC for spare parts;
- Land cost (3000  $[\frac{\$}{acre}]$ );
- Financing cost contributes to 2.7% of TPC and It comprises cost of securing financing, including fees and closing costs, but not including interest during construction;
- Other owner's costs comprise preliminary feasibility studies, economic development to incentive local collaboration, construction and/or improvement of roads/railroads near the site boundary, legal fees, permitting costs, owner's contingency. This section contributes to 15% of TPC;

Finally, the sum of all capital expenditures including their escalation during capital expenditures of three years gives the total as-spent capital costs. In fact, TOC are expressed on "base year", but financing structure starts from the start of construction. So, TASC is useful to take into account interests during construction period.

## 3.9.2 Operation and maintenance costs

These costs are caused by operating and maintaining the plant over his expected life. O&M costs include [33], [25]:

- Operating labor costs;
- Maintenance Material and Labor;
- Administrative and Support Labor;
- Consumables: cost of fuel and other consumables useful to our plant functioning;
- Co-products and by-products;

Operating and maintenance assumptions (O&M)	Parameter	value	reference
Fixed			
Labor costs	[k\$/person/year]	60	[25]
Maintenance cost	[%TPC/year]	2.5	[34]
Administrative and Support	[% O&M labor]	25	[33]
Labor			
Insurance	[% TPC/year]	1	[35]
Catalyst and sorbent			
substitution			
Reforming catalyst lifetime	[years]	5	[36]
reforming catalyst cost	[k€/m³]	50	[34]
WGS-catalyst lifetime	[years]	5	[34]
WGS-catalyst cost	[k€/m³]	14	[34]
Consumables			
Cooling water make-up cost	[€/]	0.2	[29]
process water costs	[€/m <sup>3</sup> ]	2	[34]
MEA make-up cost	[€/t]	1042	[34]
Natural gas cost	$[\epsilon/GJ_{LHV}]$	6	[29]
Electricity cost	[€/MWh]	80	[29]
CO2 transport and storage cost	[€/t]	10	[25]

#### Table 11: Main fixed and variable O&M economic assumptions

# 3.9.3 Definition of economic structure

After a general overview on the financial structure generally used to analyse power plant costs, the definition of our economic structure will be underlined thanks to a series of economic assumptions.

This analysis has the objective to estimate a specific cost for Hydrogen produced by our reforming plant [USD/kg]. A discounted cash flow (DCF) analysis will be used to evaluate economic feasibility of the entire project. In particular, an investor-owned utility (IOU) finance structure is chosen and a high-risk profile is assumed, because a carbon capture section is provided.

Before describing economic analysis, it is necessary a list of economic assumptions.

value	source
3 years	[33]
30 years	[33]
10%, 60%, 30%	[33]
45-55%	[33]
5.5-12%	[33]
15 years	[35]
15 years	[35]
38%	[33]
3.60%	[33]
3%	[33]
	value 3 years 30 years 10%, 60%, 30% 45-55% 5.5-12% 15 years 15 years 38% 3.60% 3%

Table 12: Definition of an economic structure related to the plant studied(An investor/owned utility structure was chosen)
The financial tool used in the discounted cash flow analysis is represented by net present value (NPV) defined as [35]:

$$NPV = \sum_{k=0}^{n} \frac{CF_k}{(1+i)^k}$$
 (18)

- CF: net cash flow at k-th year;
- i: discount rate;
- n: sum of operational and construction period year;

A discount rate of 10% is assumed in this study due to higher uncertainty related to reforming plant equipped with a CCS system. In fact, discounted rate is related to level of risk of the plant studied, which is different from a technology to another one [25]. The range is between 5 and 10% [25].

According to the financial study reported in [35], to calculate net cash flow with more accuracy, we have to distinguish construction and operational period.

### > Construction period

Plant construction is not instantaneous, but It requires some years. For our purposes, this period corresponds to three years and the payment of the entire capital cost occurs. So, during every year of construction period, each capital cost is escalated thanks to a nominal annual rate to find an escalated total overnight cost ( $TOC_{esc}$ ) [35].

$$TOC_{esc} = \sum_{i=1}^{Y} TOC_{esc_i} = \sum_{i=1}^{Y} TOC_i * (1 + p_{ann})^{i-1}$$
 (19)

Debt repayment starts from first year of operational period. During construction period, an amount of interests on debt  $(I_{cons})$  occurs. Adding these interests with escalated TOC, the total as-spent cost is found (TASC) [35].

$$TASC = TOC_{esc} + I_{cons}$$
(20)

$$I_{cons} = \sum_{i=1}^{Y} TOC_{esc_i} * s_d * p_d$$
(21)

About to net cash flow, during this period only negative flow occurs and It will be composed by TASC referred to specific year. Only equity share of investment will take in order to calculate net cash flow, while the part of debt share is reported only during operational period [35].

$$CF_i = -TASC * s_e \tag{22}$$

#### Operational period

During operation period, net cash flow will be formed by algebraic sum of all revenues, expenses, taxes and annuities. A brief description of each parameters will be done.

About to expenses (E), They are composed by mass and energy input streams, catalyst replacement, maintenance and insurance costs and labor [35]. Revenues (R) are formed by selling the product plant and eventually by-products. In this case, the main

product is Hydrogen and potential by-products could be electricity and heat produced in surplus. Cost associated to Hydrogen produced can be represented by two terms: cost of Hydrogen (COH) and levelized cost of Hydrogen (LCOH).

COH is the cost per [MWh] of hydrogen produced during first year of operation and then It will be escalated at a defined inflation rate [35]. LCOH is a constant cost of hydrogen produced during entire plant lifetime without escalation. Thanks to LCOH, It is possible to calculate the cost of hydrogen produced from the plant with the following equation [37]:

$$LCOH\left[\frac{\epsilon}{kg}\right] = \frac{\sum_{n=1}^{N} \frac{CAPEX_n + OPEX_n}{(1+i)^n}}{\sum_{n=1}^{N} \frac{H2 \ produced}{(1+i)^n}}$$
(23)

, where N is the plant operational period.

Annuity (AN) is a constant payment which occurs during debt repayment period. In fact, this flux is useful to repay the debt portion of the capital cost [35].

$$AN = \frac{s_d \cdot (1 + s_d)^n}{(1 + s_d)^{n-1}}$$
(24)

With the product between TASC and  $p_d$ , debt portion to repay is known. Proceeding with debt payment, interest declining. So, to know the interest for a generic year (k) [35]:

$$I_k = D_{k-1} * S_d \tag{25}$$

D<sub>k-1</sub>: part of the debt just to repay

Taxes (T) related to income of the plant will be calculated by the product between taxable income and tax rate [35]:

$$T_k = (R_k - E_k - I_k - Depr_k) * p_{inc}$$
(26)

Deprk: depreciation of plant value during plant life

#### 3.9.4 Capital cost investigation

The procedure starts with a subdivision of the entire plant into basic components. In this way, thanks to the reference from literature, total plant cost can be investigated adding installation and indirect costs.

As we can see in the table below, a list of different costs for each plant sections are related to a specific size, cost and year, which is different from our year plant. So, for each section of the plant, the erected cost (C) is derived from reference cost ( $C_0$ ) with a reference size ( $S_0$ ) by following formula [34]:

$$\frac{c}{c_0} = \left[\frac{s}{s_0}\right]^f \tag{27}$$

• s: is the actual size of component investigated;

- S<sub>0</sub>: is the reference size of the reference cost component (C<sub>0</sub>) used to investigate our specific component cost;
- f: scale factor depends on specific equipment and if estimations are not available a default value equals to 0.6 is set [35];

Moreover, there is the possibility that a reference cost for a specific component is not available. Solution consists of using equations to find the relative equipment cost. The general equations to find the equipment cost (EC) are [35]:

$$EC = PEC_0 * (B_1 + B_2 * F_M * F_p)$$
 (28)

$$(PEC_0) = k_1 + k_2 * (C) + k_3 * [(C)]^2$$
(29)

$$(F_p) = z_1 + z_2 * (P) + z_3 * [(P)]^2$$
 (30)

, where  $PEC_0$  is the cost in base conditions,  $B_1 e B_2$  are related to specific components [35].  $F_M e F_p$  are material and pressure factors and They are always major or equal than one [35]. In the second expression, constants  $k_1$ ,  $k_2 e k_3$  are related to equipment type and a purchased cost is expressed referring to base conditions (atmospheric pressure and Temperature) [35]. For this reason, the third equation accounts pressure effects, while temperature effects are included in material factor, which is reported by tables [35].

Туре	k1	k2	k3
Centrifugal	3.3892	0.0536	01538
	z1	z2	z3
	-0.3935	0.3957	-0.00226
Material	FM	B1	B2
SS	2.25	1.89	1.35

Table 13: Coefficients to find pump costs [35]

Coupling the two procedures explained to find every equipment cost, a list of all single cost is found. These costs are related to a specific year, which is generally different from reference plant year. To escalate the equipment cost based on a given year to reference plant year chosen in the economic simulation, chemical engineering plant cost index (CEPCI) is used to escalate costs [35]:

$$\frac{C_1}{C_2} = \frac{CI_1}{CI_2}$$
(31)

- C<sub>1</sub>: equipment cost at base year
- *C*<sub>2</sub>: equipment cost at chosen year
- CI: cost index from CEPCI

Table 14: List of economic assumptions related to different plant sections to calculate entire plant cost

PLANT	REFERENCE	REFERENCE	REFERENCE	SCALE	BASE	DEE
SECTION	PARAMETER	SIZE	COST [M€]	FACTOR	YEAR	NLF
Air Separation Unit	O2 produced [kg/s]	28.9	26.6	0.7	2008	[36]
Gas heated reformer-auto thermal reformer	[MW <sub>thLHV</sub> ]	400	48	0.7	2008	[34]
Shift reactors	$[MW_{th_{LHV}}]$	815.2	3.71	0.67	2008	[34]
MEA capture system	CO2 capture [kg/s]	38.4	29	0.8	2008	[34]
PSA unit	Inlet flow [kmol/h]	17069	27.96	0.6	2007	[30]
H2 compressor	Power [HP]	1	0.0012	0.82	1987	[30]
CO2 compression	Power [MW]	13	9.9	0.67	2008	[34]
Air blower	Power [MW]	47.61	14.77	0.67	2008	[34]
Expander	Power [MW]	200	33.7	0.67	2008	[34]
Heat exchangers	Heat transferred [MW]	57.2	1.8	0.9	2008	[36]

As citated in [34], the procedure to add installation costs provides a percentage of each component of the system, but this is a procedure which could not help when a comparison with unconventional plants was done. So, only two coefficients are used to account installation costs and They are 68% for power section and 80% for hydrogen and CO2 section [34]. The just mentioned percentages, applied to equipment costs, allow to find total direct plant cost (TDPC). The bare erected cost (BEC) is founded thanks to add indirect plant costs with TDPC. Indirect plant costs, as mentioned in [30], are equals to 14% of the TDPC.

Summarizing, an economic structure is schematized above to understand better the entire economic investigation presented.

Component	Cost [M€]		
Σ of all components			
Total equipment cost [TEC]	Σ of each component cost		
Direct costs (piping/valves, civil works,			
instrumentation, etc.)			
Total installation cost [IC]	80% of TEC [34]		
Total direct plant cost [TDPC]	TEC+IC		
Indirect costs [IndC]	14% of TDPC [30]		
Bare erected Cost [BEC]	TDPC+IndC		
EPCM [Engineering procurement	8% of REC		
construction manegement]	8% 01 BEC		
EPCC	BEC+EPCM		
process contingencies			
Carbon capture section	20% of section cost		
Other sections	10% of section cost		
project contingency	15% of EPP + process		
project contingency	contingencies		
Total plant cost [TPC]	EPCC+ Process and project		
	contingency		
Pre-production costs	2% of TPC		
Inventory capital	0.5% of TPC		
Land cost	3000\$/acre		
Financing cost	2.7% of TPC		
Other Owner's costs	15% of TPC		
Total overnight Cost [TOC]	TPC+ all owner's cost		

Table 15: Economic structure adopted to calculate total overnight cost (TOC)

## 4 Results

In this chapter the results obtained from model simulation on Aspen software are discussed. In order to have a general overview of the system modelled, a list of main inlet streams in the principal section of the system are reported in table above.

Table 16: Main properties and composition of major streams derived from software simulation related to overall system (composition is reported in mol%)

UNIT	NG feed	PRE- REF INLET	O2 FEED	ATR INLET	PSA INLET	AIR TO BURNER	FLUE GASES	H2 DELIVERY	CO2 CAPTURED
т [°С]	50	400	243.8	650	40	140.3	904.8	30	32
P [bar]	70	24	25	23.3	21	2.5	2	70	110
Flow [kmol/h]	1675.5	2094.4	1005.3	4720.4	5199.2	6000	6487.5	4456.3	1631.0
Flow [kg/h]	29500	37046.1	32169.8	82322.8	19247.5	173101.6	183364.8	8983.8	71010.2
Methane	91.89	73.51	0.00	36.95	0.34	0.00	0.00	0.00	0.00
Ethane	3.88	3.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Propane	2.24	1.79	0.00	0.00	0.00	0.00	0.00	0.00	0.00
i-Butane	0.07	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Butane	0.07	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00
i-Pentane	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
n-Pentane	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H2	0.00	0.00	0.00	1.48	95.23	0.00	0.00	100	0.05
H2O	0.00	20.00	0.00	59.75	0.39	0.00	8.49	0.00	1.72
CO2	0.37	0.30	0.00	1.30	3.29	0.00	3.16	0.00	98.22
со	0.00	0.00	0.00	0.02	0.30	0.00	0.00	0.00	0.00
N2	1.37	1.10	0.00	0.49	0.44	79.00	73.42	0.00	0.00
02	0.00	0.00	100	0.00	0.00	21.00	14.94	0.00	0.00

A fundamental point of this study is related to carbon capture system. To obtain detailed results, the system was simulated as a separate case. Also in this case, in the table above, composition

and main physical aspects are reported to main streams involved in the simulation.

UNIT	SYNGAS	LEAN SOLVENT	RICH AMINE	RIGENERATE AMINE	SCRUBBED GAS	CO2 CAPTURED
T [°C]	40	40	100	107.3	40.4	15
P [bar]	1.5	1.0	1.1	1.6	1.0	1.0
Flow [kmol/h]	10156	80000	84600	82969	5556	1631
Flow [kg/h]	150202	1891830	2016341	1945331	25691	71010
Methane	0.18	0.00	0.00	0.00	0.32	0.00
H2	48.76	0.00	0.00	0.00	89.11	0.05
H2O	33.22	85.42	84.32	85.94	6.79	1.72
CO2	17.46	3.78	5.47	3.64	3.08	98.22
со	0.16	0.00	0.00	0.00	0.28	0.00
N2	0.23	0.00	0.00	0.00	0.41	0.00
02	0.00	0.00	0.00	0.00	0.00	0.00
Ar	0.00	0.00	0.00	0.00	0.00	0.00
MEA AMINE	0.00	10.80	10.21	10.41	0.00	0.00

 Table 17: Main properties and composition of major streams related to CO2

 capture system simulation (composition is reported in mol%)

# 4.1 Technical results

To implement an efficient technical analysis, there is the need to compare the main results with a different system. In this way, positive and negative aspects of our plant can be underlined. The plant used as reference is just described in the 3.7. In the table below, main results of simulation are reported for both the plants.

NG feed         [t/h]         29.5         22.7           NG fuel         [t/h]         -         6.6           Oxygen feed         [t/h]         32.2         -           Process water         [m³/h]         92.5         92.9           INPUT         -         -         -           NG thermal input (LHV)         [MW]         394         391.2           OUTPUT         -         -         -           H2 thermal output         [MW]         300         300           CO2 captured (MEA system)         [t/d]         1704         1170.6           CO2 vented         [t/d]         216         695.3           REFORMING SECTION         -         -         -           Reformer Temperature         [°C]         1023         890           H2/CO ratio in syngas         [mol/mol]         2.9         5.4           H2/CD vield in the reformer         [mol/mol]         2.1         3.2           POWER BALANCE         -         -         -           ASU         [MW]         3.7         -         -           CO2 compressors and pumps         [MW]         3.7         -         -           CO2 compressors and pump
NG fuel         [t/h]         -         6.6           Oxygen feed         [t/h]         32.2         -           Process water         [m³/h]         92.5         92.9           INPUT         Image: Second Seco
Oxygen feed         [t/h]         32.2         -           Process water         [m³/h]         92.5         92.9           INPUT         Import         Import         Import           NG thermal input (LHV)         [MW]         394         391.2           OUTPUT         Import         Import         Import           H2 thermal output         [MW]         300         300           CO2 captured (MEA system)         [t/d]         11704         1170.6           CO2 vented         [t/d]         216         695.3           REFORMING SECTION         Import         Import         Import           Reformer Temperature         [°C]         1023         890           H2/CO ratio in syngas         [mol/mol]         2.9         5.4           H2/CH4 yield in the reformer         [mol/mol]         2.1         3.2           POWER BALANCE         Import         Import         Import           ASU         [MW]         3.7         -           CO2 compressors         [MW]         3.7         -           CO2 compressors and pumps         [MW]         5.9         6.0           Blower         [MW]         31.7         35.3
Process water         [m³/h]         92.5         92.9           INPUT         IIII INPUT         IIIII INPUT         IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII
INPUT         Implement         Implement         Implement           NG thermal input (LHV)         [MW]         394         391.2           OUTPUT         Implement         Implement         Implement           H2 thermal output         [MW]         300         300           CO2 captured (MEA system)         [t/d]         1704         1170.6           CO2 captured (MEA system)         [t/d]         216         695.3           CO2 vented         [t/d]         216         695.3           REFORMING SECTION         Implement         Implement         890           H2/CO ratio in syngas         [mol/mol]         2.9         5.4           H2/CO ratio in syngas         [mol/mol]         2.1         3.2           POWER BALANCE         Implement         Implement         Implement           ASU         [MW]         8.6         -           Oxy-compressors         [MW]         3.7         -           CO2 compressors and pumps         [MW]         5.9         6.0           H2 compressors         [MW]         5.9         6.0
NG thermal input (LHV)         [MW]         394         391.2           OUTPUT
OUTPUT         Image: Method of the system         Image: Method of th
H2 thermal output         [MW]         300         300           CO2 captured (MEA system)         [t/d]         1704         1170.6           CO2 vented         [t/d]         216         695.3           REFORMING SECTION
CO2 captured (MEA system)         [t/d]         1704         1170.6           CO2 vented         [t/d]         216         695.3           REFORMING SECTION
CO2 vented         [t/d]         216         695.3           REFORMING SECTION </td
REFORMING SECTION         Image: margin syngas         [°C]         1023         890           H2/CO ratio in syngas         [mol/mol]         2.9         5.4           H2/CH4 yield in the reformer         [mol/mol]         2.1         3.2           POWER BALANCE         Image: margin synthesis
Reformer Temperature         [°C]         1023         890           H2/CO ratio in syngas         [mol/mol]         2.9         5.4           H2/CH4 yield in the reformer         [mol/mol]         2.1         3.2           POWER BALANCE
H2/CO ratio in syngas         [mol/mol]         2.9         5.4           H2/CH4 yield in the reformer         [mol/mol]         2.1         3.2           POWER BALANCE              ASU         [MW]         8.6         -           Oxy-compressors         [MW]         3.7         -           CO2 compressors and pumps         [MW]         7.5         5.4           H2 compressors         [MW]         5.9         6.0           Blower         [MW]         31.7         35.3
H2/CH4 yield in the reformer         [mol/mol]         2.1         3.2           POWER BALANCE         -         -         -           ASU         [MW]         8.6         -           Oxy-compressors         [MW]         3.7         -           CO2 compressors and pumps         [MW]         7.5         5.4           H2 compressors         [MW]         5.9         6.0           Blower         [MW]         31.7         35.3
POWER BALANCE         Image: Marcine State           ASU         [MW]         8.6         -           Oxy-compressors         [MW]         3.7         -           CO2 compressors and pumps         [MW]         7.5         5.4           H2 compressors         [MW]         5.9         6.0           Blower         [MW]         31.7         35.3
ASU         [MW]         8.6         -           Oxy-compressors         [MW]         3.7         -           CO2 compressors and pumps         [MW]         7.5         5.4           H2 compressors         [MW]         5.9         6.0           Blower         [MW]         31.7         35.3
Oxy-compressors         [MW]         3.7         -           CO2 compressors and pumps         [MW]         7.5         5.4           H2 compressors         [MW]         5.9         6.0           Blower         [MW]         31.7         35.3
CO2 compressors and pumps         [MW]         7.5         5.4           H2 compressors         [MW]         5.9         6.0           Blower         [MW]         31.7         35.3
H2 compressors         [MW]         5.9         6.0           Blower         [MW]         31.7         35.3
Blower [MW] 31.7 35.3
Water pump         [MW]         0.1         0.1
Syngas expander [MW] -15.9 -15
NG expander [MW] -0.6 -0.7
Steam turbine [MW] -26 -41.5
Import(+)/export(-) electricity [MW] 15 -10.4
PERFORMANCE INDEXES
m <sub>na ea</sub> [kg/s] 8.7 7.8
n,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
<sup>1</sup> /H <sub>2</sub> [%] 76 76.6
$\eta_{H_2,eq}$ [%] 71.4 80.3
<i>E<sub>CO2</sub></i> [gCO2/MJth] 6.4 20.6
<i>E<sub>CO2,eq</sub></i> [gCO2/MJth] 10 21.5
<i>CCR</i> [%] 87.9 60.8
<i>CCR<sub>eq</sub></i> [%] 82.5 63.7
Specific consumption $[MJ/Nm_{H_{2}}^{3}]$ 14.1 13.9
Specific CO2 capture $[Kg/Nm_{H_{-}}^{3}]$ 0.7 0.48
Specific CO2 emission $[Kg/Nm_{H_{2}}^{3}]$ 0.10 0.29

#### Table 18: List of all general inputs, outputs and technical indexes

As for the overall system results, in the Table 19, MEA system simulation results are reported.

FLOW	UNIT	ATR	Reference
Syngas flow	[kmol/s]	2.82	2.2
CO2 concentration	[%mol]	17.5	14.1
ABSORBER			
Lean-solvent temperature	[°C]	40	40
Column Pressure	[bar]	1.1	1.1
Number of stages	[n°]	5	5
Column diameter	[m]	10	10
Lean solvent	[molCO2/mol MEA]	0.35	0.35
STRIPPER			
Rich solvent	[molCO2/mol MEA]	0.53	0.52
Rich-amine temperature	[°C]	100	100
Column Pressure	[bar]	2.1	2.1
Number of stages	[n°]	10	8
Column diameter	[m]	5	5
Heat required	[GJ/t CO2]	3.8	3.95
MEA make up	[kg/h]	8.59	36.9
CO2 captured	[%]	90.3	90.1

Table 19: List of CO2 capture system simulation results

### 4.1.1 Technical comparison

Other than performance indexes, material and energy balance of the selected plants are presented in the Table 18. Concerning on Hydrogen efficiency  $(\eta_{H_2})$ , both the plants present almost the same values. Referring to base case without CO2 capture, SMR presents higher energy efficiency than ATR. Moreover, when a carbon capture system is added to SMR, higher steam to carbon ratio occurs to achieve more CO conversion. In this way, higher concentration of CO2 in the mole flow is obtained and a more efficient removal process occurs. On the other hand, more heat is required from furnace causing a higher consumption of natural gas. For this reason, a reduction of hydrogen efficiency occurs. The power balance shows that ATR plant has the necessity to import electricity from external grid at the contrary of reference plant. This represents an important advantage related to SMR respect with ATR. This is principally caused by two reasons. First one is related to the production of oxygen at high pressure. The sum of ASU and oxygen consumes covers 21% of the total electricity required from ATR plant. The second reason is related to the heat available at the end of the processes. Due to high electricity consumption of the process, entire amount of available heat is used to produce high pressure steam. In this way, throw an expansion of the steam in a turbine, an electricity production occurs. There is a markable difference of heat available between the plants at favour of SMR. In case of SMR plant, the electricity produced overpassed consumes and an export to the grid occurs. On the contrary, an electricity import is necessary to ATR plant. This is principally caused by air separation unit. For these reasons, the important difference between the equivalent efficiencies are explained. The overall CO2 captured is described by CCR. In case of ATR, 87.9% of the CO2 produced is captured respect with 60.8% related to SMR plant, so a marked difference occurs. This is cause by the SMR reformer design. In fact, after hot gases cooling exiting from furnace, they are vented to the atmosphere. An important amount of CO2 contained in these gases causes low overall CO2 capture. From an environmental point of view, ATR represents a more promising technology than SMR. Specific emission parameters,  $(E_{CO_2})$  and  $(E_{CO_2,eq})$ , are similar to CCR, but they describe CO2 emissions to heat contained into the natural gas entering the plant. Obviously, higher values are obtained in case of SMR respect with ATR due to the highest CO2 emissions. Both the plants present almost the same specific consumption, because the total natural gas entering plants is almost equal.

In the Table 19, main results from MEA simulation on Aspen are reported. The most important result is related to energy consumption to regenerate amine in the scrubber column. In case of ATR, 3.8 [GJ/tCO2] are required to regenerate amine respect with 3.95 [GJ/tCO2] required in SMR case. This is due to lower CO2 concentration in syngas came from reforming section of SMR, which requires more lean solvent than ATR case. Both the plants achieve a carbon capture removal of 90%.

### 4.2 Economical results

To understand the real feasibility of a plant, It has to find the cost of the final product. Economic structure is described in the Table 12 of section 3.9.3. About to capital costs investigation, in the section 3.9.4, a detailed description is reported with the objective to find a final overall cost called total as-spent capital cost (TASC) as reported in table below.

Table	20:	<b>Economic</b>	results	of	the	plant
-------	-----	-----------------	---------	----	-----	-------

Capital cost investigation	ATR PLANT [M€]	REFERENCE PLANT [M€]
Air Separation Unit (ASU)	11.0	-
Gas heated reformer-auto thermal reformer (GHR+ATR)	44.7	51.1
HTS+LTS (shift reactor)	2.1	2.1
MEA CO2 capture system	15.9	11.9
PSA unit	14.1	14.7
H2 compressor	1.9	2.0
CO2 compressor and condenser	6.4	5.2
Blower	10,6	11.4
Expander	6,0	0.7
Heat exchangers	3.1	5.1
Steam turbine	8.9	12.1
Water pump	0.2	0.1
TOTAL EQUIPMENT COST (TEC)	125.0	116.4
Installation cost		
Power Island	86.6	82.7
CO2 capture and H2 section	38.4	33.7
Total installation cost	89.6	83.2
TOTAL DIRECT PLANT COST (TDPC)	214.5	199.5
Indirect cost	30.0	27.9
BARE ERECTED COST (BEC)	244.6	227.5
EPCM [Engineering procurement construction management]	19.6	18.2
EPCC	264.1	245.7
Process contingencies		
Reforming section	8.7	8.3
CO2 capture and H2 section	7.7	16.5
Project contingencies	42.1	40.6
TOTAL PLANT COST (TPC)	322.6	286.2
Pre-production costs	6.5	5.7
Inventory capital	1.6	1.4
Land cost	0.3	0.3
Financing cost	8.7	7.7
Other Owner's costs	48.4	42.9
TOTAL OVERNIGHT COST [TOC]	388.0	344.4

The TOC founded are expressed in constant currency. During capital expenditure period, throw specific multipliers define in the section 3.9.3, costs escalation and interests on debt are adding to TOC to find TASC.

[M€]	ATR	REFERENCE
ETOC	388	344
IDC	9.6	8.5
TASC	398	353

Table 21: Calculation of TASC during expenditure period

During plant functioning, fixed and operating costs have to be accounted to calculate the net cash flow for every year. In the Table 11, a list of assumptions has been defined to calculate these costs, which are reported in the table below. Fixed costs are constant during all operation period, while operating cost are related to plant availability defined in the section 3.4.3.

Fixed cost [M€/year]	ATR PLANT	<b>REFERENCE PLANT</b>
Labor costs	1.3	1.3
Maintenance cost	8.1	7.2
Administrative and Support Labor	0.3	0.2
Insurance	3.2	2.9
TOT fixed	13.0	11.6
Catalyst replacement	0.3	0.3
Cooling water	7.5	4.8
process water costs	10.9	15.3
MEA make-up cost	0.1	0.3
Natural gas cost	74.4	73.9
CO2 transport and storage cost	6.2	4.3
electricity	10.4	-
TOT operating	109.9	98.9
OPEX	122.8	110.5

Table	22:	0&M	costs
-------	-----	-----	-------

By the use of capital costs (CAPEX) and operating cost (OPEX), It is possible to find how much is the cost to produce 1 [kg] of hydrogen. This cost is represented by LCOH, which is defined in equation (23). As we can expected, reference plant shows a lower hydrogen production cost than ATR plant. These costs are reported in the table below and They are expressed in union dollars<sup>1</sup> to have a better comparison with costs reported in literature.

CASE	TASC [M€]	O&M[M€/year]	LCOH [USD/kg]
ATR case study	397.7	122.8	1.86
Reference plant	352.9	110.5	1.67

Table 23: Main economic results related to selected plants

Figure 13 helps to understand how different costs contribute to total hydrogen production cost. So, a cost partitioning between CAPEX, OPEX and natural gas cost is underlined. Production cost is dominated by fuel cost, which covers 53% and 59% of the total cost of ATR and SMR respectively.

<sup>&</sup>lt;sup>1</sup>1[€] = 1.11[2016 USD] (<u>https://www.macrotrends.net/2548/euro-dollar-exchange-rate-historical-chart</u>)



Figure 13: Different contributes to LCOH

On the other hand, to find the minimum hydrogen selling price, a discounted cash flow analysis is used, where all revenues, expenses, interests and taxes are taken in account. Minimum hydrogen selling price is founded fixing the return of investment at last year of plant life. In this case a major difference between ATR and SMR occurs. Concerning on ATR plant, a minimum hydrogen selling price of 2.27 [USD/kg] is founded, which is higher than 1.79 [USD/kg] in SMR case, substantially caused by the high difference on electrical balance.

#### 4.2.1 Economic comparison

In this section, a comparison between ATR and SMR economic results will be investigated. The following figures are useful to understand better cost differences between the selected plants. Both the plants were subdivided in general sections to understand better every contribute on capital cost expenditure. These contributes are reported in the figure below.



Figure 14: Contributes to overall capital plant cost

In the H2 plant costs were reported: all reforming section costs, WGS costs, steam turbine costs and hydrogen separation and compression. The marked difference between SMR and ATR plant is caused by two reason principally. The first one is due to the cost of reformer. As reported in the Table 20, SMR reformer presents a cost 15% higher than ATR cost. The second reason is due to difference in electricity production by steam turbine. A higher production is achieved in case of SMR plant respect with ATR one. Concerning on PSA and compression unit, costs are substantially the same as reported in the Table 15, because both the plants have the same hydrogen output. Moreover, the little difference on PSA cost is due to a higher mole flow in SMR case. The cost difference regard to MEA system is only due to the quantity of CO2 captured. Both the MEA capture systems installed in the selected cases provide to a 90% of CO2 capture

contained in the mole flow. In case of ATR, higher CO2 mole flow is contained in the syngas exiting from WGS section respect with SMR. Consequently, MEA system installed in ATR plant has the highest cost, because It captures more CO2 than SMR one. In fact, the criteria chosen to find MEA capture cost in the Table 14 is related to CO2 captured rate. Moreover, the presence of an air separation unit in the ATR plant constitutes the major contribute which bring to have highest capital costs respect with SMR. As performance, ASU for technical causes important an disadvantage on economic comparison too. ASU cost contains both the ASU costs and oxy-compressor costs. Referring to ATR plant only, this cost cover almost the 10% of the total ones.

Operating and maintenance costs are related to functioning of the plant and they are important to define the net cash flow in the discounted cash flow analysis. Consulting Figure 15 and Figure 16, where OPEX for both the plants are reported, some differences can be easily noted.



Figure 15: List of contributes to OPEX in case of ATR plant



Figure 16: List of contributes to OPEX in the reference plant case

As reported in Table 22, fixed costs are the same, because they are referred to assumptions reported in the Table 11. Concerning on operating costs, the substantially difference is due to electricity cost. In case of SMR, the availability of an electricity surplus corresponds to a potential revenue and no expenditures are needed. On the contrary, in ATR plant the electricity import from external grid represents an operating cost.

### 4.3 Sensitivity Results

In the next figure, effects of price variations on LCOH will be reported. Sensitivity analysis has been done for both the plants. Obviously, the most cost variation is due to the increment on natural gas cost. Figure 18 illustrates a decrement on LCOH in reference plant case, because the higher cost of electricity implies a higher revenue derived from electricity export. In the ATR plant, a major capture od CO2 occurs respect with SMR one.

So, variations on CCS costs cause a higher increment on LCOH in case of ATR plant.



Figure 17: Range of LCOH according to natural gas cost variations



Figure 18: Range of LCOH according to electricity cost variations



Figure 19: Range of LCOH according to CCS cost variations



Figure 20: Effect of "Carbon tax" on LCOH

Figure 20 shows that an autothermal plant with CCS system becomes a better solution respect with SMR at high CO2 emission costs. Nowadays, carbon tax is just limited at low values, but in the next future It could be easily very high, because the objective of an energetic sustainability grid is becoming more and more important around major world's countries.

## 5 Cost comparison

In this chapter a comparison with other cost reported in external literature is investigated. It is difficult to assess an optimal comparison, because there are a series of uncertainties related to economic assumptions done when external works are used. Moreover, It is necessary to compare results obtained with standard cost to understand better the real feasibility of plant investigated. To do that, there are a series of agency which, every year, public detailed information over the entire energy chain. This comparison will focus on information reported by "International Energy Agency" (IEA) and "Sustainable Gas Institute" (SGI) throw detailed report.

In the IEA report for Tokyo G20 [3], It is reported an overview on hydrogen production cost for different countries around the world. These costs present important differences, because they are strictly related to fuel and electrical costs, which can change a lot from a country to a different one. Generally, Hydrogen produced by a plant with CCS system is more expensive than a traditional one due to the presence of a capture system and costs related to transport and storage of CO2 separated. The range of hydrogen production cost is between 1.5 and 3 [USD/kg], while in case of renewables sources use a higher range between 2.5 and 6 [USD/kg] is achieved [3]. Consulting these costs with economic results of the plant reported in Table 23, autothermal reforming plant with CCS system could represent a valid alternative at traditional plant based on SMR, because high CO2 carbon capture rate can be achieved with a limited amount in hydrogen production cost. In fact, with a LCOH of 1.86 [USD/kg], ATR falls in the range of low-cost hydrogen production technology. In the report of "SGI" [38], a detailed analysis on possible retail price to consumers has been leaded. Final retail price is composed by a series of unit costs. The most important contributes is related to hydrogen production cost (40-50%) [38]. So, minimising gas production cost leads to an important reduction on retail gas price. Best opportunities to achieve these reductions are related to improve technical efficiencies and reduce penalty efficiencies caused by CCS system [38]. The use of existing transport and storage infrastructure added a contribute of 35% of the total price [38]. However, these costs are affected by uncertainty due to lack of information about to length and capacity of pipeline infrastructure [38]. Remaining costs are related to storing captured CO2, taxes, profits and administrative costs [38]. The average retail gas price founded by "SGI" referred to UK market, is around 9 pence per kWh [38], which corresponds to 4.78 [USD/kg]<sup>2</sup>. Applying the percentage mentioned above, an average gas production cost of 2.15 [USD/kg] is founded and, if compared with value obtained in ATR, there is a positive marginal cost which could conduce to higher profits. Uncertainty about costs is related to a series of specific considered. factors directly related to plant Geographical location, presence of an existent pipeline, distance from CO2 storage site other than fuel and electricity prices can influence a lot the final price. In case of a new hydrogen pipeline, "IEA" estimates a cost of 1 [USD/kg] over a distance of 1,500 [km]

<sup>&</sup>lt;sup>2</sup> 1[GBP2016] = 1.35[USD 2016] (<u>https://www.macrotrends.net/2549/pound-dollar-exchange-rate-historical-chart</u>)

[3]. Referring to high-scale hydrogen infrastructure, pipeline represents the best transport choice in case of long distances and large volume transported [3]. Summarizing, a general discussion on actual average cost related to hydrogen infrastructure has been presented. However, costs investigated present wide range of estimates. These uncertainties should be reduced by use of demonstration projects.

#### 6 Conclusions

A detailed discussion between autothermal reforming and steam methane reforming plant has been investigated in this thesis to understand how a carbon capture system influences a commercial reforming plant. Both of reforming sections are conducted at high pressure to have a better H2/CO ratio in the reformer and to improve the system design. The use of an absorption capture system based on amine permits to separate CO2 at ambient pressure causing a penalty in the successive compression before to put inside a pipeline. On the contrary, high pressure syngas entering the PSA unit allows to enhance the H2 compression. Steam methane technology presents higher hydrogen efficiency than autothermal reformer one due to the difference on how reforming reaction occurs. Moreover, when a carbon capture system is added at the plant, variations on hydrogen efficiency favours autothermal reforming plant. In fact, in case of SMR, higher steam to carbon ratio has to be provided in the reforming section to achieve high CO conversion causing a major request of sensible heat with a consequently increment on natural gas consumption. Both the plants have an availability of heat, which is used to produce steam to employ in a steam power cycle. The electricity produced is used to satisfy all the power requests from the plant. Concerning on SMR plant, a surplus of electricity produced to export to external grid is achieved. On the contrary, ATR should be import electricity causing higher expenses. The production of oxygen at high pressure constitutes both technical and economical penalty respect with SMR. Moreover, there is an important difference on the final cost of hydrogen at favour of SMR plant. Applying a carbon tax, this cost difference is reduced until to the hydrogen production cost of SMR overpass the ATR one. Both the plants analysed are based on mature technology to produce hydrogen and separate CO2. From a technical and environmental point of view, autothermal plant presents higher potentialities than SMR. Moreover, H2 production from autothermal reforming with CCS system will become economical competitive throw an important growth of the Carbon tax.

#### 7 References

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