

Available online at www.sciencedirect.com

Energy Procedia 4 (2011) 1125–1132

**Energy
Procedia**

www.elsevier.com/locate/procedia

GHGT-10

Application of the Sorption Enhanced-Steam Reforming process in combined cycle-based power plants

Matteo C. Romano^{a*}, Eugenio N. Cassotti^a, Paolo Chiesa^a,
Julien Meyer^b, Johann Mastin^b

^a Politecnico di Milano, Energy Department, via Lambruschini 4, 20156 Milano, Italy

^b Institute for Energy Technology, Environmental Technology Department, Instituttveien 18, 2007 Kjeller, Norway

Abstract

Sorption Enhanced-Steam Methane Reforming (SE-SMR) is a promising process which allows producing in a single reactor a hydrogen-rich syngas from natural gas, while capturing the CO₂ by reaction with a solid sorbent. Scope of this paper is to investigate the potentiality of the SE-SMR process coupled to a combined cycle, by estimating the plant performance and by discussing the main issues related to plant layout and reactors characteristics. The calculated net efficiency and carbon capture ratio are comparable with that obtained for a competitive technology based on Auto-thermal Reforming (ATR), but advantages could result from the higher plant simplicity and lower plant cost.

© 2011 Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).

Keywords: SE-SMR; reforming; hydrogen; calcium oxide; fluidized bed; CO₂ sorption.

1. Introduction

Capture of CO₂ in fossil fuels-fired power plant can be accomplished by means of several different strategies. Pre-combustion separation technologies usually imply a three stage fuel processing sequence where:

1. the primary feedstock is first converted at high temperature into a synthesis gas stream where carbon is mainly in form of carbon monoxide (CO);
2. most of the heating value of the syngas is reallocated from CO to H₂ through an intermediate temperature, catalytically activated water gas shift reaction, which at the same time converts CO to CO₂;
3. removal of CO₂ from syngas is accomplished at ambient temperature by means of proper selective solvents.

This arrangement suffers from two important drawbacks: (i) plant complexity due to the presence of different sections each designated to perform one single processing stage; (ii) different temperature levels for each stage, implying syngas cooling which in turn requires extensive heat transfer surfaces and brings about a significant conver-

* Corresponding author. Tel.: +39-02-23993846; fax: +39-02-23993913.

E-mail address: matteo.romano@polimi.it

sion efficiency decay. A substantial improvement would instead be achieved if all these stages could be compacted into a single step. This can be obtained for instance by subtracting CO₂ from the gaseous phase during the syngas generation process, which in turn significantly enhances conversion of CO to CO₂ due to removal of the reaction product. This paper investigates how this concept can find practical application when natural gas is used as primary feedstock and CO₂ removal is carried out by reaction with calcium oxide through a Sorption Enhanced-Steam Methane Reforming (SE-SMR) process.

The full potential of the SE-SMR technology is reached by integrating the reforming technology with a high temperature fuel cell. The solid oxide fuel cell has an operation temperature up to 1100°C and the excess of heat from the SOFC is ideal for the regeneration process. When these two technologies are integrated, the heat from the fuel cell is used for upgrading natural gas to hydrogen and essentially no energy is wasted.

The aim of this paper is discussing the potentiality of a combined-cycle based power plant, where the hydrogen-based syngas produced in a SE-SMR process is burned in a combustion turbine. Such a plant, leading worse performance than the SOFC-based one, can however be a good option for short mid-term applications due to its good performance and relatively simple layout with respect to competitive technologies.

2. Sorption Enhanced-Steam Methane Reforming

2.1. Thermodynamic principles

The following steam methane reforming (SMR) reaction:



is the reference for hydrogen production from natural gas in mid and large scale plants. Since reforming reaction is highly endothermic and the moles of products are more than reactants, elevated temperatures and low pressures favor high conversion degrees.

The most common reforming process employed in industrial practice is based on fired tubular reformers (FTR). In these reactors, part of the inlet natural gas is burned in a furnace to provide the heat of reaction, mainly through radiative heat transfer. To achieve high methane conversions, an adequate steam excess compared to stoichiometry of reaction 1 is provided along with a process temperature around 900°C, which in turn requires high alloy austenitic steels capable of tolerating wall temperatures up to 1050°C [1]. Another option for H₂ production from natural gas is the use of auto-thermal reformers (ATR). In such reactors, oxygen (introduced as air or rich O₂ mixtures) is used as reactant to promote exothermic oxidation reactions, providing heat for steam reforming reaction without any need of heat exchange surfaces.

When a carbon-free synthesis gas is required, for example in low CO₂ emission power plants, carbon monoxide generated by the reforming reaction is converted into H₂ and CO₂ according to the water gas shift (WGS) reaction (2):



Usually, two WGS reactors with intermediate cooling are employed, in order to: (i) combine high CO conversion in the colder reactor with faster kinetics in the hotter one and (ii) recover with a higher efficiency the heat of reaction after the first WGS reactor, which is available at high temperature (400-500°C).

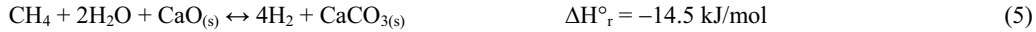
An option to obtain high methane to hydrogen conversions in a single step is removing one of the reaction products from the gaseous phase. In Sorption Enhanced-Steam Methane Reforming (SE-SMR) processes, CO₂ is adsorbed over a solid sorbent while SMR and WGS reactions occur. Therefore, progression of the gaseous phase reactions (1-2) is not limited to equilibrium set by CO₂ formation and proceed almost to a complete depletion of reactants. A promising sorbent for SE-SMR applications seems to be calcium oxide, which can react with CO₂ generating CaCO₃ according to the following carbonation reaction (3):



Being (3) a gas-solid reaction, a definite CO₂ partial pressure, function of temperature, establishes in the gas phase at chemical equilibrium. Equation (4), reported in [3] and obtained from thermo-chemical data in [2], is an example of equation expressing the increase of equilibrium CO₂ partial pressure with temperature:

$$p_{\text{CO}_2,eq} [Pa] = 4.137 * 10^{12} * \exp(-20474/T) \quad (4)$$

The overall calcium-based SE-SMR reaction, which results from the single reactions (1), (2) and (3), is reported in eq.(5):



The enthalpy balance of the overall reaction (5) is only -14.5 MJ/kmol , meaning that it is well thermally balanced, and therefore not only the carbonation reaction facilitates hydrogen production by removing CO_2 from the gaseous phase, but also provides the heat required for the steam reforming reaction, allowing for the use of adiabatic reactors, or at least with limited heat duties.

The influence of the SE-SMR operating parameters has been predicted by chemical equilibrium considering pure methane as primary fuel and over-stoichiometric amounts of CaO , so that adsorption of gaseous species is not limited by CaO availability. Hydrogen yield (defined as the moles of hydrogen generated per mole of methane, whose

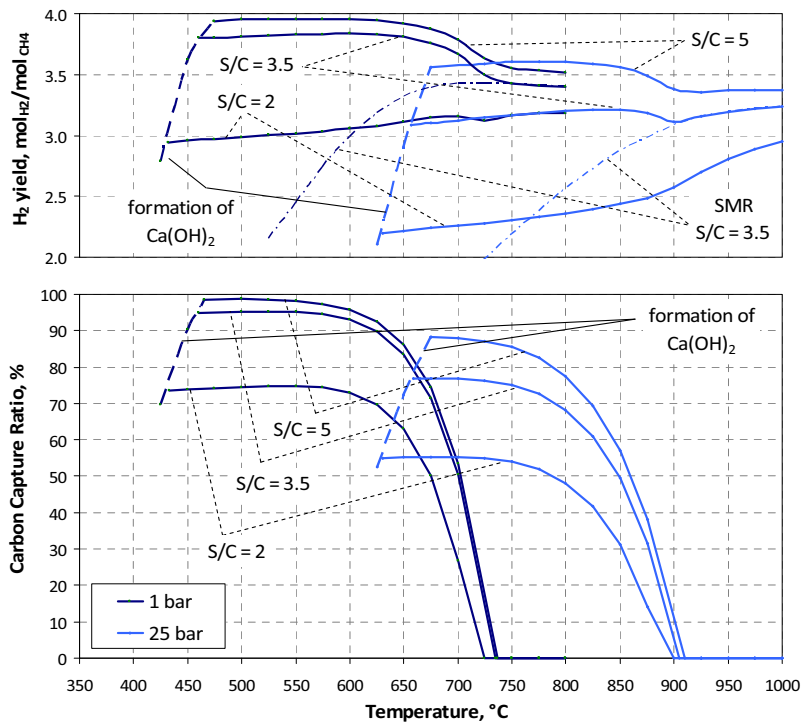


Figure 1 – Influence of temperature, pressure and steam to carbon ratio on hydrogen yield and CO_2 capture ratio in a SE-SMR process. The dot dashed curves in the upper diagram refer to a conventional SMR process carried out at 3.5 steam to carbon ratio.

maximum value is 4 as given by reaction 5) and carbon capture ratio (CCR, defined as the moles of C adsorbed by calcium oxide per mole of methane to the reformer) are shown in Fig.1. Considering one of the curves in the graph, at given pressure and S/C, a temperature range can be identified where H_2 yield and CCR experience limited variations. In this range, effects of temperature on SMR, WGS and carbonation reactions counterbalance. At higher temperatures, the equilibrium CO_2 partial pressure of the carbonation reaction increases (eq.4) and a higher CO_2 fraction will be hence present in the gaseous phase, leading to lower CaCO_3 formation and carbon capture ratio hence decreases. Despite the lower CO_2 sorption, CH_4 conversion increases, provided that exothermic SMR reaction is favoured, while H_2 yield varies depending on the SMR and

WGS equilibria. By further increasing temperature, a point is reached where the CO_2 pressure in the gaseous phase is below that predicted by eq.4 and no CO_2 can be adsorbed by generating CaCO_3 . At such temperatures, no sorption occurs and reactions behave like in conventional steam reformers.

By reducing temperature below the flat zone section, a point is reached where steam in the gaseous phase reacts with calcium oxide producing solid Ca(OH)_2 . Similarly to carbonation reaction (3), the reaction:



exhibits an equilibrium of steam partial pressure in the gas phase, whose value increases with temperature. Accordingly, when the steam partial pressure in the stream exceeds the equilibrium threshold, H_2O reacts with CaO until that value pressure establishes. Therefore, at low temperature a significant fraction of steam is removed from the gaseous phase and effective S/C ratio reduces limiting the advancement of SMR and WGS reactions and leading to lower H_2 yields and CCR.

Effects of S/C ratio and absolute pressure are also outlined in Fig.1. Despite its beneficial effect over carbonation reaction, a pressure increase prevents obtaining high conversion degrees in the SMR reaction (where the number of moles of products is greater than the one of reactants) and it leads to lower H₂ yields and CCR for a given temperature and S/C ratio. For sake of comparison, curves of H₂ yield for a conventional steam reforming process are also reported in Fig.1, highlighting the benefits due to SE-SMR in a wide range of operating temperatures.

On the basis of this picture, it is possible to affirm that with a calcium-based SE-SMR system, high H₂ yields and CO₂ separation can be carried out in a single step, at temperatures much lower than required by conventional reformers.

An important issue to consider in SE-SMR processes is sorbent regeneration. In fact, once-through processes are impractical due to the huge amount of sorbent required for CO₂ capture in large power stations which poses dramatic hurdles in term of availability, handling and cost. Sorbent regeneration is carried out via calcination reaction (the reverse of reaction 3), which is obtained by reducing CO₂ partial pressure in the gaseous phase below the CO₂-CaCO₃ equilibrium value set by eq. (4). This result can be obtained either by reducing the actual CO₂ partial pressure (pressure swing) or by increasing temperature and hence equilibrium pressure (temperature swing). In any case, thermal power is required in the calcination step to provide the heat required by the endothermic calcination reaction. Heat can be provided either by means of heat exchangers or by direct combustion in the calciner. In the second case, which is the only practical possibility when high temperatures are needed, calcination has to be carried out by means of oxy-fuel combustion to avoid dilution of the CO₂ released from calcination with nitrogen.

2.2. Current state of the technology

Sorption-enhanced steam methane reforming (SE-SMR) has been successfully demonstrated in laboratory scale with natural Ca-based sorbents (calcite and dolomite) both in fixed bed reactors [4,5] and in fluidized bed reactors [6,7]. Moreover, extensive research work on the development of diverse high temperature synthetic CO₂-sorbents suited for the SE-SMR process has been carried out by many authors. The main motivations are the improvement of the multi-cycle ability, absorption capacity and mechanical stability as well as to lower the regeneration temperature of these new sorbents compared to natural Ca-based calcite or dolomite. Lithium zirconate has been proposed due to its lower regeneration temperature than Ca-based sorbents [8]. However, it shows too slow sorption kinetics for low CO₂ partial pressures. Sodium zirconate shows better kinetics but the presence of sodium poisons the Ni-catalyst during the high temperature regeneration step. Lithium silicate was seen as a promising material but thermodynamics limits the hydrogen yield compared to Ca-based sorbents [9]. Therefore, most of the work carried out recently focuses on novel supported Ca-based materials, mainly due to the good availability of Ca-precursors, their lower cost, and the satisfactory kinetic properties of the carbonation reaction [11,12].

Extensive work has also been carried out in the field of reactor and process modeling adapted to the SE-SMR process for H₂-production, showing the potential of this technology [13-15]. However, SE-SMR in a continuous production mode still needs to be demonstrated at a level making possible a further promising up-scaling.

2.3. Reactors for large scale power plants

The conventional steam methane reforming processes (SMR) at industrial scale are operated at pressures between 15 and 40 bar. Operating the SE-SMR process in a continuous mode involves the transport of large amounts of solids (CO₂-sorbent and reforming catalyst) between two dedicated reactors: a reformer/carbonator and a calciner. The transport of this large quantity of solids can be achieved by using two interconnected fluidized bed reactors in various configurations. However, fluidized bed technology with circulation of solids involves quite low pressure difference between the reactors. This means, in turn, that operating the SE-SMR reformer in the 15-40 bar pressure range, two alternatives can be devised for the calciner: (i) a process operating at about the same pressure but at temperature far above 1000°C, (ii) a process operating at lower pressure and temperature which in turn requires a challenging device, like a lock-hopper for example, to move the sorbent between the reformer and the calciner.

When considering a large size SE-SMR process operating at high pressure, a number of elements must be considered related to heat transfer, hydrodynamic regime and reactors size. At the conditions encountered in the plant assessed and described in the next paragraph, the CO₂ partial pressure at the calciner outlet is equal to 15.4 bar, requiring a calcination temperature of at least 1110°C according to eq.4.

At such a temperature, two options are possible: decrease the CO₂ partial pressure or provide heat by means of an oxy-fuel combustion. CO₂ partial pressure can be lowered by adopting an atmospheric calciner, which would lead to technical challenges for the pressurization of high temperature solids in the reformer, or by diluting the calciner gas with steam, leading to significant efficiency penalties (for example, to reduce calcination temperature by 100°C in the assessed case, steam should be added at a rate more than 3 times the CO₂ on a molar basis).

For these reasons, a high temperature calciner seems preferable, where heat for calcination is provided by natural gas oxy-combustion. Other issues should be considered under these conditions related to catalyst and sorbent deactivation at high temperature. Considering the sorbent, a material pre-treated at high temperature (around 1200°C) should be used to increase its mechanical properties and resistance to attrition. Natural limestones for example show stable long term absorption capacities around 8 to 10 gCO₂/100g sorbent which is suitable for continuous operation in a fluidized bed reactor system with circulation of solids. As far as catalyst is concerned, the presence of oxygen, even in relatively small amounts, can cause oxidation if a conventional nickel catalyst is used and exposure to high temperatures could reduce its activity. One solution is to use noble metal catalyst, which would increase the catalyst cost. If the reformer is a transport (riser) reactor, a particle segregation by size and density could be another option to avoid transporting the catalyst to the calciner and increase catalyst lifetime: the denser and bigger catalyst particles would stay in the dense phase of the riser and the sorbent particles would be entrained. Finally, another option would be to introduce internals (tubes for example) in the reformer (preferably bubbling in that case), coated with active material in small quantities.

When operating the calciner at high pressure, thermal power needed to heat the solids up to calcination temperature increases. In order to reduce fuel consumption in the calciner, it is important to preheat the solids with the sensible heat in the CO₂-rich gaseous stream released from the calcination zone. This could be carried out by adopting a moving bed reactor, where solids and gas are in contact in a countercurrent flow leading to an efficient heat transfer. However, in moving bed reactors, low gas velocities are required to avoid bubble formation and particles mixing, and very large reactor footprints would hence result. For this reason, reactors operating in bubbling or fast fluidization regimes should be preferred in large plants to limit costs. The option considered in this work is a circulating fluidized bed calciner, with a suspension preheater (Fig. 2). Such a preheater is a direct contact heat exchanger widely used in plants for cement production, where solids and gas flowing in countercurrent are contacted and separated in 4 to 6 cyclones in series. The solids entering at the top of the system descend through the cyclones and are heated up, being suspended in the hotter gas stream flowing upwards.

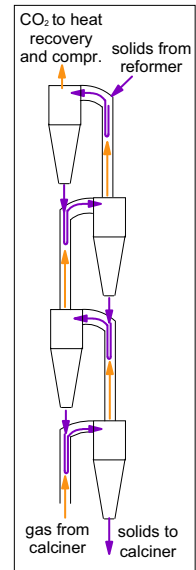


Figure 2 Suspension preheater.

3. Combined cycle-based power plant

The layout of the assessed plant is shown in Fig. 3. Reformer and calciner are transport reactors working at 25 bar. Under transport regime, reaction kinetics can be a limiting parameter and a proper dimensioning is required to operate close to chemical equilibrium as here assumed. Reformer operates at 700°C, with a S/C ratio of 4.5 in order to obtain an overall carbon capture ratio (i.e. also considering CO₂ from natural gas oxy-combustion) close to 90%. Steam for reforming is partly added by means of NG humidification in a saturator, where low temperature heat from CO₂ cooling is efficiently used, limiting the losses associated with steam extraction from the steam cycle. Calcination temperature was set equal to 1200°C, about 90°C higher than the equilibrium temperature at the CO₂ partial pressure at calciner outlet.

Calcium oxide utilization was set equal to 15%, which means that carbonated sorbent contains 15% CaCO₃ and 85% CaO on a molar basis. Considering that unreacted CaO exiting the reformer behaves as inert material circulating between the reactors and increases the calciner heat duty and the natural gas burned under oxy-fuel conditions, the higher the calcium utilization the higher the plant efficiency. The assumed carbonation level is higher than maximum conversion reported in [17] for natural sorbent experiencing a very large number of carbonation-calcination cycles, but seems reasonable if thermal pretreatment, doping [18,19] or steam reactivation [20] are assumed for novel Ca-based materials. Further studies on sorbent properties under SE-SMR process conditions are however required to understand the feasible carbonation level. No sorbent blow-down was considered despite it

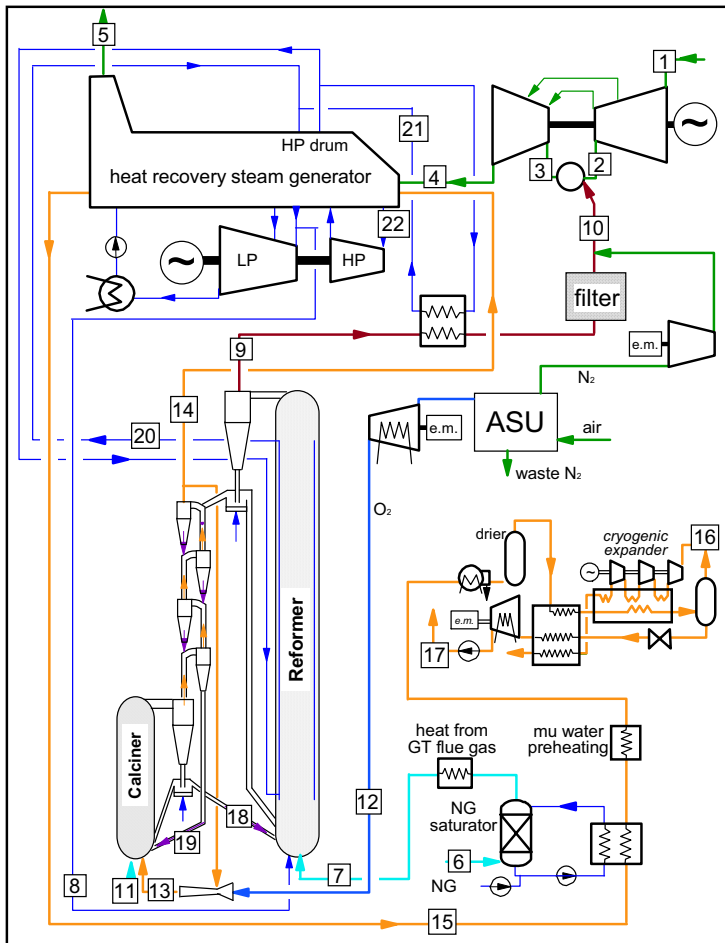


Figure 3 Layout of the assessed SE-SMR-based combined cycle.

selected ΔT of 2°C in the heat exchanger, with the contribution of the cooling energy coming from the reheating of the incondensable gases, during their 3 stage expansion to atmospheric pressure. The purified CO₂ stream is then compressed to 90 bar and then pumped to 150 bar.

The hydrogen-rich fuel from the SE-SMR process is diluted with N₂ from ASU for NO_x control and burned in a state-of-the-art GE 9FB gas turbine. Nitrogen flow rate for dilution was calculated to obtain a stoichiometric flame temperature of 2300 K, which should be low enough to have acceptable NO_x emissions without post-combustion selective catalytic reduction (SCR) [23]. Mass and energy balances were evaluated by means of the GS (Gas-Steam cycles) code [24], developed at the Department of Energy at Politecnico di Milano. For CO₂ compression and conditioning, where real fluid effects occur, the commercial tool Aspen Plus[®] was used [25], with Peng-Robinson equation of state. GS code is a powerful and flexible tool that can be used to predict the performance of a wide variety of chemical processes and systems for electricity production. The gas turbine performance on syngas were calculated by means of a simulation model [26] calibrated on the basis of a real plant data [16]. With respect to the natural gas fired machine, TIT was reduced by 30°C when firing the SE-SMR fuel to keep the same blade temperature of the design case, as predicted by the calculation model. Before combustion, the hydrogen-rich syngas from the reformer is cooled down to 500°C and filtered to remove solid particles entrained from SE-SMR process. The heat recovery steam cycle is based on a three pressure levels (130/27/4 bar, 565/565°C) steam generator. Reheat pressure was matched with the reformer pressure, so that steam for reforming can be extracted from hot-RH outlet.

would increase the average sorbent activity, because the consequent CaCO₃ make-up would also lead to efficiency penalties for its initial calcination.

In order to avoid excessively high local temperatures in the calciner, O₂ for combustion is diluted to 40%vol by recycling part of the gas stream from the suspension preheater. Recycle is carried out at high temperature to limit thermodynamic losses. An ejector, driven by pressurized O₂ (stream 12), is used to allow the recycle and the required oxygen pressure was calculated by means of specifications from an industrial manufacturer [21]. A stand alone ASU (Air Separation Unit) producing a 97% purity O₂ stream with an electric consumption of 200 kWh/t of pure O₂ is considered. While higher O₂ purities reduce the amount of incondensable gases in the final CO₂, relevant ASU cost and electric consumption increases will result in obtaining higher purities [22].

After cooling and heat recovery, the CO₂ rich stream is conditioned with a cryogenic process to the specified purity of 96%mol and compressed at the liquid state. Low purity CO₂ stream is liquefied at -42°C and incondensable gases are separated from liquid CO₂ (stream 16). The cooling duty for liquefaction is obtained by evaporation of the purified CO₂, throttled to attain the

4. Results

The main results of the simulation are reported in Tab. 1 and 2. Power balance can be compared with the reference Natural Gas-fired Combined Cycle (NGCC) without CO₂ capture and a competitive plant with pre-combustion CO₂ capture based on Auto-Thermal Reforming (ATR) and Methyl Di-Ethanol Amine (MDEA) technologies [16].

A net plant efficiency of 50.2% was obtained, 8.4% points less than the reference NGCC, with about 88% CO₂ capture, resulting in a specific emission of 14% of the NGCC plant. A higher gas turbine power was obtained as a result of the lower air flow rate compressed, consequence of the low calorific value of the steam-rich fuel burned. Because of the large amount of steam required in the reformer, a similar steam turbine power was calculated, despite the additional steam generated outside the HRSG, from CO₂-rich stream, GT fuel and carbonator cooling.

Oxygen production and compression require the largest amount of auxiliary power: almost 26 MW_e, equivalent to an efficiency penalty of 2.7% points. Power for carbon dioxide compression and conditioning is equal to 5.1 MW_e, a rather low value as a consequence of the high pressure of the CO₂-rich stream exiting the calciner.

Results obtained for the SE-SMR-based plant can be compared with the competing technology based on ATR and CO₂ capture with MDEA. Performance of two reference cases are reported in Tab. 1 [16]: a “base case” calculated by considering advanced components and assumptions aimed at efficiency maximization (at the today’s best available technology) and a “simplified case” where a simpler layout (e.g. lower fuel temperature at GT combustor inlet) and lower cost components (e.g. adiabatic pre-reformer instead of a heat exchanger pre-reformer) were considered. Efficiency of the SE-SMR-based plant is almost the same as the ATR+MDEA “base case”. It hence lies in the higher efficiency range 48.2–50.7% estimated for the reference technology. On the other hand, a slightly lower carbon capture ratio was obtained for the SE-SMR-based plant leading to almost 40% higher CO₂ emissions.

Table 1 – Power balance of the assessed SE-SMR case and reference NGCC and ATR+MDEA plants.

	NGCC	SE-SMR	ATR+MDEA “base”	ATR+MDEA “simplified”
Electric power, MW				
Gas turbine	273.4	316.1	287.7	289.0
Gas turbine auxiliaries	-0.96	-1.11	-1.01	-1.01
Steam turbine	150.7	148.7	157.2	217.7
Steam cycle pumps	-1.98	-2.86	-3.17	-3.68
Auxiliaries for heat rejection	-2.31	-2.02	-2.89	-3.97
ASU	-	-14.75	-	-
O ₂ compressor / Air boost compressor	-	-8.99	-7.09	-10.54
N ₂ compressor	-	-10.83	-	-
MDEA process auxiliaries	-	-	-3.58	-4.31
CO ₂ compression	-	-5.10	-15.14	-18.00
Net power, MW _e	418.8	419.2	412.0	465.1
Net efficiency, %	58.59	50.19	50.65	48.18
Cold Gas Efficiency, %	-	83.09	88.87	79.78
Carbon Capture Ratio, %	-	87.96	91.56	91.71
Specific emission, g _{CO2} /kWh	350.2	49.2	34.2	35.3

Table 2 – Temperature, pressure, flow rate and composition of the main plant streams, shown in Fig.2.

point	G kg/s	T, °C	p, bar	M kmol/s	Molar composition, %											
					CH ₄	C ₂₊	CO	CO ₂	H ₂	H ₂ O	O ₂	N ₂	Ar	He	CaO	CaCO ₃
1	571.3	15.0	1.01	19.80				0.03		1.04	20.73	77.28	0.92			
2	455.1	419.8	18.36	15.77				0.03		1.04	20.73	77.28	0.92			
3	519.1	1416	17.81	19.94				0.54		25.18	9.05	64.50	0.73			
4	635.3	617.0	1.04	23.97				0.46		21.12	11.01	66.65	0.76			
6	13.38	15.0	30.00	0.71	82.88	10.38		1.10				5.49		0.15		
9	46.27	700.0	25.00	4.82	1.88		0.11	0.15	53.16	43.87		0.81		0.02		
11	5.54	15.0	30.00	0.29	82.88	10.38		1.10				5.49		0.15		
13	55.08	579.1	26.04	1.65				35.92		21.54	40.00	0.61	1.91	0.02		
14	55.91	775.0	25.00	1.63				59.87		35.90	2.00	1.00	1.20	0.03		
17	43.15	38.5	150.0	0.99				96.12			2.01	0.69	1.17	0.01		
18	247.4	1200		4.41											100	
19	276.5	911.4		4.41											85.00	15.00

5. Conclusions

The potential of the Sorption enhanced-Steam Methane Reforming coupled with a state-of-the-art combined cycle was assessed in this work. A net efficiency of 50.2% and 88% carbon capture ratio were calculated for the proposed layout, in line with performance of a competitive plant based on ATR and pre-combustion CO₂ absorption. Advantages for the assessed plant could result from a higher plant simplicity and lower cost. A sensitivity analysis on the main design parameters and sorbent properties, and an economic assessment are necessary to fully understand the potential of this concept.

References

- [1] Aasberg-Petersen K, Bak Hansen J-H, Christensen TS, Dybkjaer I, Seier Christensen P, Stub Nielsen C, Winter Madsen SEL, Rostrup-Nielsen JR. Technologies for large-scale gas conversion. *Applied Catalysis A: General*, 2001, 221:379-387.
- [2] García-Labiano F, Abad A, de Diego LF, Gayán P, Adánez J. Calcination of calcium-based sorbents at pressure in a broad range of CO₂ concentrations. *Chem Eng Sci* 2002, 57:2381-2393.
- [3] Barin I. Thermochemical data of pure substances. Weinheim: VCH, 1989.
- [4] Li Z, Cai N, Yang J. Continuous production of hydrogen from sorption-enhanced steam methane reforming in two parallel fixed bed reactors operated in a cyclic manner. *Ind Eng Chem Res* 2006, 45:8788-8793.
- [5] Harrison DP. Calcium enhanced hydrogen production with CO₂ capture. *Energy Procedia* 2009, 1:675-681.
- [6] Hildenbrand N, Readman J, Dahl IM, Blom R. Sorbent enhanced steam reforming (SESR) of methane using dolomite as internal carbon dioxide absorbent: Limitations due to Ca(OH)₂ formation. *Appl Catal A: General* 303, 2006, 131-137.
- [7] Johnsen K, Ryu HJ, Grace JR, Lim CJ. Sorption-enhanced steam reforming of methane in a fluidized bed reactor with dolomite as CO₂-acceptor. *Chem Eng Sci* 2006, 61:1195-1202.
- [8] Ochoa-Fernandez E, Rønning M, Grande T, Chen D. Synthesis and CO₂ capture properties of nanocrystalline lithium zirconate. *Chem Mater* 2006, 18:6037-6046.
- [9] Kato M, Yoshikawa S, Nakagawa K. Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations. *J Mater Sci Lett* 2002, 21:485-487.
- [10] Escobedo Bretado M, Guzmán Velderrain V, Lardizábal Gutiérrez D, Collins-Martínez V, Lopez Ortiz A. A new synthesis route to Li₄SiO₄ as CO₂ catalytic/sorbent. *Catal Today* 2005, 107-108:863-867.
- [11] Martavaltzi CS, Lemonidou AA. Development of new CaO based sorbent materials for CO₂ removal at high temperature. *Micropor Mesopor Mat* 2008, 110:119-127.
- [12] Mastin J, Meyer J. Novel calcium-based regenerative sorbents for high temperature CO₂-capture. 1st Meeting of the High Temperature Solid Looping Cycles Network, IEA Greenhouse Gas R&D Programme, 15-17 September 2009, Oviedo, Spain. www.co2captureandstorage.info/networks/looping1.htm.
- [13] Johnsen K, Grace JR, Elnashaie SSEH, Kolbeinsen L, Eriksen D. Modeling of sorption-enhanced steam methane reforming in a dual fluidized bubbling bed reactor. *Ind Eng Chem Res* 2006, 45:4133-4144.
- [14] Lee DK, Baek IH, Yoon WL. A simulation study for the hybrid reaction of methane steam reforming and in situ CO₂ removal in a moving bed reactor of a catalyst admixed with a CaO-based CO₂ acceptor for H₂ production. *Int J Hydrogen Energ* 2006, 31:649-657.
- [15] Koumpouras GC, Alpay E, Lapkin A, Ding Y, Štěpánek F. The effect of adsorbent characteristics on the performance of a continuous sorption-enhanced steam methane reforming process. *Chem Eng Sci* 2007, 62:5632-5637.
- [16] Romano MC, Chiesa P, Lozza G. Pre-combustion CO₂ capture from natural gas power plants, with ATR and MDEA processes. *Int J Greenh Gas Con* 2010, 4:785-797.
- [17] Grasa GS, Abanades JC. CO₂ capture capacity of CaO in long series of carbonation/calcination cycles. *Ind Eng Chem Res* 2006, 45:8846-8851.
- [18] Manovic V, Anthony EJ. Thermal activation of CaO-based sorbent and self-reactivation during CO₂ capture looping cycles. *Environm Sci Technol* 2008, 42:4170-4174.
- [19] Manovic V, Anthony EJ, Grasa G, Abanades JC. CO₂ looping cycle performance of a high purity limestone after thermal activation/doping. *Energy & Fuels* 2008, 22:3258-3264.
- [20] Manovic V, Anthony EJ. Steam Reactivation of Spent CaO-Based Sorbent for Multiple CO₂ Capture Cycles. *Environ Sci Technol* 2007, 41:1420-1425.
- [21] Körting Reference Data for Application of Jet Ejectors and Vacuum Processing, 1997.
- [22] Wilkinson MB, Boden JC, Panesar RS, Allam RJ. CO₂ capture via oxyfuel firing: optimisation of a retrofit design concept for a refinery power station boiler. *Proceedings of the First National Conference on Carbon Sequestration*, Washington DC, USA, 2001.
- [23] Chiesa P, Lozza G, Mazzocchi L. Using hydrogen as gas turbine fuel. *J Eng Gas Turb Power* 2005, 127:73-80.
- [24] Software Presentation: GS (Gas-Steam cycles). 2010. www.gecos.polimi.it/software/gc.html
- [25] Aspen Plus version 2006.5, Aspen Technology, Inc., Cambridge, Massachusetts U.S.A.
- [26] Chiesa P, Macchi E. A thermodynamic analysis of different options to break 60% electric efficiency in combined cycle power plants. *J Eng Gas Turb Power* 2004, 126:770-785.