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Pre-combustion packed bed chemical looping (PCCL) technology for efficient H₂-rich gas production processes

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HIGHLIGHTS

- A novel process based on chemical looping for H₂/N₂ syngas production has been presented.
- The experimental proof of principle has been carried out in a 2 kW packed bed reactor.
- A Fe-based OC has been tested in the range 600–800 °C.
- The PCCL system has an electrical efficiency up to 51.5%.

GRAPHICAL ABSTRACT

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ABSTRACT

A novel reactor system is presented and investigated for the production of a hydrogen rich gas stream for power or ammonia production, based on pre-combustion chemical looping (PCCL) technology using dynamically operated packed bed reactors. In this process, the oxygen carrier (OC) is alternately oxidized with a gas mixture of air and steam to produce a H₂/N₂ product gas stream combining oxidation by air and water-splitting, and subsequently reduced with syngas producing a concentrated CO₂ stream. The process is carried out at elevated pressure, but at intermediate temperature (in the range of 600–900 °C), which allows circumventing the extremely high temperatures required in chemical-looping combustion. In addition, the N₂/H₂ gas stream can be produced at the required composition for ammonia production, rendering this process also competitive with the conventional ammonia production. A preliminary experimental study has been carried out in a 2 kW_{th} packed bed reactor using an iron-based oxygen carrier. The influence of the operating temperature and the initial solid composition during the oxidation cycle on the H₂-rich gas yield has been investigated. The complete reduction to pure iron reduces the reactivity of the material due to sintering, whereas a controlled reduction to wüstite (FeO) allows to maintain a higher stability of the material, although the oxygen capacity is decreased.

A preliminary thermodynamic assessment of the integrated PCCL plant for power production with natural gas has been carried out reaching an electrical efficiency of 49–51.5% (depending on the plant arrangement) with a carbon capture rate above 95%. The main parameter affecting the plant performance was found to be the steam requirement during the oxidation cycle. The comparison with benchmark technologies has confirmed the potential of the PCCL system.

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Nomenclature

AGR	acid gas removal	PCCL	pre-combustion chemical looping
AR	air reactor	PSA	pressure swing adsorption
BOP	balance of plant	Red	reduction phase
CCS	carbon capture and storage	SC	steam cycle
CGE	cold gas efficiency, $Q_{LHV, \text{syngas}}/Q_{LHV, \text{coal}}$	SEM	scanning electron microscopic analysis
CLC	chemical looping combustion	SH//RH	superheated/reheated
CPU	CO ₂ process unit	SPECCA	specific primary energy consumptions for CO ₂ avoided, MJ _{LHV} /kg _{CO2}
EDX	energy dispersive X-ray analysis	ST	steam turbine
FR	fuel reactor	TGA	thermogravimetric analysis
GT	gas turbine	TIT	turbine inlet temperature
HP-IP-LP	high-intermediate-low pressure	TOT	turbine outlet temperature
HR	heat removal phase	WGS	water gas shift
HRSC	heat recovery steam cycle		
HRSG	heat recovery steam generator		
HT-IT-LT	high-intermediate-low temperature		
IC	Inter-cooled		
IGCC	integrated gasification combined cycle		
LHV	lower heating value, MJ/kg		
MEA	mono-ethanol-ammine		
NG	natural gas		
NGCC	natural gas combined cycle		
OC	oxygen carrier		
Ox	oxidation phase		
PBR	packed bed reactor		

Symbols and units

cp	gas/solid heat capacity J/kg-K
m	mass flow rate, kg/s
Q_{LHV}	thermal power, MW _{TH}
N	molar flow rate, kmol/s
p	pressure, bar
T	temperature, °C
E_{CO2}	CO ₂ specific emissions, kg _{CO2} /MWh _E
ΔT	temperature difference, °C
η_{el}	net electric efficiency

1. Introduction

Reduction of greenhouse gas emissions is one of the most important challenges that the power industry will face in the next decades [1]. Carbon capture and storage (CCS) technologies could cut by at least one order of magnitude the CO₂ emissions from fossil fuel-fired power plants. CO₂ capture technologies can be applied according to three main configurations: (i) post-combustion capture for flue gases, (ii) pre-combustion capture producing carbon-free H₂-based fuel for a power cycle and (iii) oxy-combustion, generating a highly concentrated CO₂ stream after water condensation. All these concepts lead to energy efficiency penalties in the order of 10–15 percentage points when implemented with the current commercially available technologies [2].

Pre-combustion CO₂ capture technologies are based on different conversion processes that occur in series. Starting from the pre-treatment of the primary fuel, the production of the syngas is typically carried out by steam reforming or coal gasification. The syngas, rich in H₂ and CO, is then mixed with steam and fed to the water gas shift (WGS) reactors to convert the CO into H₂ and CO₂. This process is normally carried out at two temperature levels to improve both the thermal efficiency, which is favored by operating a high temperature WGS stage at around 320–500 °C allowing to recover the heat of reaction by high pressure steam production, and the CO conversion, which is favored at lower temperature (around 185–300 °C) due to the chemical equilibrium constraint. The shifted fuel is then sent to the cold acid gas removal unit where CO₂ and sulfur species are removed by absorption. The CO₂ desorption is carried out by thermal regeneration using low pressure (LP) steam in the reboiler of the desorber column or by pressure reduction in flash chambers where the CO₂ is released and sent to the compressors train. Pre-combustion separation processes are well known in the industry and widely adopted for the production of H₂ and chemicals (i.e. ammonia); a great research effort is nowadays devoted to demonstrate the feasibility of this system also for clean power production by using a H₂-fuelled gas

turbine combined with a steam cycle for an efficient thermal integration. Natural gas power plants integrated with pre-combustion CO₂ capture systems have been presented in recent years reaching an energy efficiency penalty of 9–12 percentage points with respect to the reference natural gas combined cycle [3–5], while in case of IGCC, the CO₂ capture integration costs about 7–11 percentage points [6–10]. Also ammonia plants use fossil fuels as primary feedstock that is decarbonized in order to produce a gas mixture of H₂/N₂ that is fed to the ammonia synthesis plant operated at high pressure (150–300 bar) and temperature in the range of 350–550 °C [11]. About 30% of the energy losses are determined by the several conversion and separation steps required [12,13] in case of natural gas. Moreover, the high capital cost of an ammonia plant is mostly associated to the costly H₂ production unit rather than the ammonia synthesis plant.

Among the different technologies that have been discussed and presented for CCS, chemical looping combustion (CLC) represents one of the most viable solution to achieve a very high CO₂ reduction with a reduced energy penalty [14]. CLC uses a metal oxide (called oxygen carrier, OC), which is oxidized in contact with air and afterward reduced (releasing the oxygen) in the presence of a reducing agent, such as a fuel: the CO₂ contained in the exhaust gases from the reduction reactions is nitrogen-free and thus easily separated at high purity after water condensation. Different oxygen carrier materials have been proposed for the CLC operation [15,16]. From an energy point of view, the oxidation reaction is always exothermic and the O₂-depleted air is produced at high temperature while the reduction reaction can be exothermic or endothermic depending both on the materials used as OC and the fuel type/composition.

For the application of CLC several different studies have been published in recent years mainly based on a pressurized circulating fluidized bed reactor (CFBR) operated with natural gas [17–19] or sulfur-free syngas from a coal gasification unit as fuel for the CLC loop operated at high pressure [20,21] (Fig. 1a). The performance of the plants studied varied from 43 to 52% for a hundreds-MW

Fig. 1. Chemical looping combustion reactor concepts based on (a) interconnected fluidized bed, (b) packed bed and (c) chemical looping for hydrogen production using moving beds.

power plant in case of natural gas as primary feedstock, depending on the configuration, assumptions and materials used. In case of a coal-fired power plant, the electric efficiency approaches 40%. CLC with coal as primary fuel can be accomplished at atmospheric pressure by converting the coal directly in a CLC fuel reactor [22–25] and 42% of net electric efficiency can be predicted for a fully integrated plant with an overall efficiency penalization of 2.5 percentage points [26]. High pressure operation with interconnected fluidized bed reactors is a challenging and unproven technology especially for the limits associated to the solids circulation. Therefore, dynamically operated packed bed reactor technology for CLC has been recently proposed and studied [27–30], where the solids remains stationary in the reactor and the gaseous streams are sequentially switched (Fig. 1b). Although a high performance is expected [31], this configuration requires for a large-scale power plant a large number of HT-switching valves and CLC reactors placed in parallel particularly because of the large number of reactors required for the heat removal phase [32].

A different approach is the combination of chemical looping and the steam-iron process (chemical looping hydrogen production), where the metal oxide is first fully reduced in a fuel reactor and after that it is oxidized in two separate reactors, where the Fe/FeO is converted into Fe_3O_4 by reaction with steam to produce pure H_2 and subsequently with air to complete the oxidation to Fe_2O_3 [33–36]. The integration of the steam-iron process has been discussed also for power and H_2 co-production using natural gas [37,38] or solid fuels [39–41]. The reactor loop is based on two counter-current moving bed reactors as shown in Fig. 1c (respectively the fuel and steam reactors) allowing for higher iron-oxide conversion compared to fluidized bed reactors, while achieving complete fuel conversion. This system has been proposed and extensively studied mostly at the Ohio State University [42,43]. Bohn et al. [44] and Lorente et al. [45] have proposed a steam-iron process using packed beds reactors: Bohn et al. have successfully demonstrated the three-stage chemical looping for combined pure hydrogen production and CO_2 capture in a reactor 10.2 mm diameter and 20 cm length (using 20 g of Fe_2O_3) while Lorente

et al. have discussed the steam iron process in a packed bed reactor as a means for H_2 storage.

This paper discusses the development of an innovative pre-combustion capture process based on chemical looping which converts a fuel stream into a H_2/N_2 rich stream. Compared to previous concepts already discussed, in this new process oxidation with steam and the air oxidation occur simultaneously. The process proposed in this paper includes the primary fuel combustion, the conversion into a H_2/N_2 stream as an intermediate product and the inherent CO_2 separation in a single reactor loop which can be carried out at high pressure and intermediate temperature (600–900 °C) resulting in a concept with a strong process intensification. The novel characteristics of this process, compared to other processes previously presented, are briefly summarized as follows: (i) a H_2/N_2 mixture is produced suitable for ammonia production as well as pre-combustion capture technologies; (ii) the reactor and OC experience a smaller temperature rise compared to packed bed reactors where the temperature rise associated with the oxygen carrier oxidation is very high (especially in the presence of an Fe-based OC) and due to the thermal stresses associated to the cycling operation the mechanical properties of the particles could easily deteriorate; (iii) the temperature rise associated with the air oxidation favors the kinetics of H_2O dissociation via the steam-iron reaction; (iv) the combination of steam and air oxidation reduces the number of reactors required and associated auxiliaries, which also represent a relevant cost of previous chemical looping concepts (i.e. HT valves, HT piping); (v) feeding air with H_2O would also result interesting for the application of HAT (humid air gas turbine); In fact the amount of high pressure steam to the process can be significantly reduced by saturating air and therefore increasing the water content during a multistage compression [46]. A HAT cycle is also particularly interesting and efficient at smaller scale applications and the operating conditions are advantageous also for the pre-combustion chemical looping technology.

The aim of this paper is to present a new process leading to the combined production of H_2/N_2 in a single reactor to be used for CO_2 -free electricity production and/or NH_3 synthesis. The paper

is structured in two main parts: (i) in the first part the experimental analysis is carried out on a Fe-based oxygen carrier to study the gas–solid redox reactions and the thermal behavior; (ii) in the second part, the effect of PCCL integration in a large scale power plant is presented in order to discuss the main issues associated to the energy penalties, the comparison with other technologies and the related advantages.

The first part of the paper is related to the description of the concept with a special focus on the main advantages and requirements for the OC and the reactor design. Subsequently, an experimental investigation with a lab-scale packed-bed reactor is presented in order to show the feasibility of the concept and to provide a preliminary proof-of-principle. This analysis includes experimental testing at both particle and reactor level. A 20 wt% Fe_2O_3 (supported with Al_2O_3) has been tested in a TGA using CH_4 diluted with CO_2 . A small packed bed reactor with 4.4 g of supported Fe_2O_3 has been used for breakthrough experiments under isothermal conditions. Finally, a medium scale reactor (500 g of particles) using pure iron as oxygen carrier physically mixed with clay as inert material has been used to evaluate the dynamic thermal behavior of the system. Additionally, a preliminary assessment of a fully integrated PCCL plant for power production using natural gas as feedstock is presented and compared with benchmark technologies providing a complete mass and energy balance of the system.

2. Description of the PCCL technology

A schematic representation of the PCCL concept is shown in Fig. 2. Two (or more) packed bed reactors are filled with a specific oxygen carrier that is alternately converted into MeO (during oxidation) and reduced to Me (during the reduction). During the reduction cycle a gaseous fuel (natural gas or syngas derived from coal/biomass/residuals gasification) is directly converted into CO_2 and H_2O , avoiding N_2 dilution and a pure CO_2 stream can be obtained after H_2O condensation. During the oxidation cycle, a mixture of H_2O and air converts the Me into MeO via oxidation with O_2 and H_2O -splitting producing a stream of H_2/N_2 (+ unreacted H_2O), that is further converted into chemicals or used as fuel for a combined cycle.

2.1. Oxygen carriers

The rational selection and design of the oxygen carrier material is essential for the exploitation of the PCCL concept. Nowadays, the

oxygen carriers for chemical looping combustion are designed in order to achieve high selectivity towards CO_2 and H_2O during the reduction in combination with high thermal, mechanical and chemical stability, reduced cost and durability over many cycles and thousands of hours under severe conditions.

For the PCCL concept, it is important that the OC provides sufficiently fast kinetics during the reduction cycle and accomplish a high conversion and selectivity during the oxidation with both O_2 and H_2O . Fe-based oxygen carriers are also reactive towards CH_4 although the kinetics are much slower than for Cu-based oxygen carriers. Some detailed analysis in term of oxygen carrier performance in the presence of methane has been discussed by several authors [47–49] using different support materials and reactor geometries and in this study we have also investigated the reactivity of CH_4 during the reduction cycle.

As for the chemical looping hydrogen production, an oxygen carrier with several thermodynamically favorable phase changes can be used for this purpose [44,50,51]. Most of the research on OC design for H_2 production has been devoted to Fe-based oxygen carriers. Iron oxides have been successfully deposited on e.g. high surface area alumina supports in an attempt to prevent excessive sintering during reduction, however, the formation of more complex structures makes the chemistry of the system more complex [52]. A different OC is represented by Fe-containing perovskites which are also defined as non-stoichiometric oxides, in which

Table 1

Main reactions considered for the PCCL process.

Gas–solid reactions	Heat of reaction	
$\text{H}_2 + 3\text{Fe}_2\text{O}_3 \rightarrow \text{H}_2\text{O} + 2\text{Fe}_3\text{O}_4$	$\Delta H^\circ_{298} = -5.8 \text{ kJ/mol}_{\text{H}_2}$	R1
$\text{CO} + 3\text{Fe}_2\text{O}_3 \rightarrow \text{CO}_2 + 2\text{Fe}_3\text{O}_4$	$\Delta H^\circ_{298} = -46.98 \text{ kJ/mol}_{\text{CO}}$	R2
$\text{CH}_4 + 12\text{Fe}_2\text{O}_3 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{Fe}_3\text{O}_4$	$\Delta H^\circ_{298} = 141.63 \text{ kJ/mol}_{\text{CH}_4}$	R3
$\text{H}_2 + \text{Fe}_2\text{O}_3 \rightarrow \text{H}_2\text{O} + 2\text{FeO}$	$\Delta H^\circ_{298} = 38.42 \text{ kJ/mol}_{\text{H}_2}$	R4
$\text{CO} + \text{Fe}_2\text{O}_3 \rightarrow \text{CO}_2 + 2\text{FeO}$	$\Delta H^\circ_{298} = -2.72 \text{ kJ/mol}_{\text{CO}}$	R5
$\text{H}_2 + \frac{1}{3}\text{Fe}_2\text{O}_3 \rightarrow \text{H}_2\text{O} + \frac{2}{3}\text{Fe}$	$\Delta H^\circ_{298} = 32.92 \text{ kJ/mol}_{\text{H}_2}$	R6
$\text{CO} + \frac{1}{3}\text{Fe}_2\text{O}_3 \rightarrow \text{CO}_2 + \frac{2}{3}\text{Fe}$	$\Delta H^\circ_{298} = -8.21 \text{ kJ/mol}_{\text{CO}}$	R7
$\text{H}_2\text{O} + 3\text{FeO} \leftrightarrow \text{H}_2 + \text{Fe}_3\text{O}_4$	$\Delta H^\circ_{298} = -60.56 \text{ kJ/mol}_{\text{H}_2\text{O}}$	R8
$\text{H}_2\text{O} + \frac{3}{4}\text{Fe} \leftrightarrow \text{H}_2 + \frac{1}{4}\text{Fe}_3\text{O}_4$	$\Delta H^\circ_{298} = -37.77 \text{ kJ/mol}_{\text{H}_2\text{O}}$	R9
$\text{O}_2 + 4\text{FeO} \rightarrow 2\text{Fe}_2\text{O}_3$	$\Delta H^\circ_{298} = -560.5 \text{ kJ/mol}_{\text{O}_2}$	R10
$\text{O}_2 + 4\text{Fe}_3\text{O}_4 \rightarrow 6\text{Fe}_2\text{O}_3$	$\Delta H^\circ_{298} = -471.96 \text{ kJ/mol}_{\text{O}_2}$	R11
CATALYTIC REACTIONS		
$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3\text{H}_2 + \text{CO}$	$\Delta H^\circ_{298} = 206.16 \text{ kJ/mol}_{\text{CH}_4}$	R12
$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO}$	$\Delta H^\circ_{298} = 247.30 \text{ kJ/mol}_{\text{CH}_4}$	R13
$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$	$\Delta H^\circ_{298} = -41.14 \text{ kJ/mol}_{\text{CO}}$	R14

Fig. 2. The concept of the pre-combustion chemical looping (PCCL) technology.

Fig. 3. Different consecutive cycles of reduction (15% H₂ + 15% H₂O) and oxidation (air + H₂O) at 800 °C in an atmospheric pressure TGA.

Fig. 4. Solid conversion during the oxidation cycle using an air/H₂O (45/55) mixture at 800 °C for several consecutive cycles.

the amount of H₂ recovered during the oxidation with H₂O is not strictly determined by the oxygen chemical potential of the phase change [53]. An oxygen carrier stability test has been carried out using an unsupported Fe-based oxygen carrier. The experiments have been carried out with a Fe-based OC. The OC particles have been obtained by milling and sieving the iron oxide (>95% of FeO) which was originally in big pellets and after preparation, they were separated in a range of 1–1.5 mm of particle diameter. The kinetics and stability of the oxygen carrier has been investigated by thermogravimetric analysis (for the description of the TGA set-up the reader is referred to Ortiz et al. [54]. The main reactions considered for an Fe-based OC are listed below (Table 1):

The reduction cycle has been carried out at 800 °C using 15% H₂ and diluted with 15% H₂O (balance N₂) to ensure a proper conversion from hematite (Fe₂O₃) to wüstite (FeO). The TGA results show the good stability of the oxygen carrier after repeated cycles (Fig. 3), although the oxidation reaction is faster in the first cycle and decreases in subsequent cycles most likely due to structural change in the material. (Fig. 4).

More detailed research on the OC is required to better understand the fundamental mechanisms (viz. solid conversion and catalytic properties of the oxygen carriers, structure-property-performance relationships, effects of parameters during manufacturing) and improve the redox kinetics modeling in order to further optimize the OC and obtain full fuel conversion during the reduction cycles and produce a H₂-rich gas with the desired H₂/N₂ composition during the oxidation cycle suitable for power or ammonia production.

A synthetic Fe-based oxygen carrier, prepared by wet impregnation on Al₂O₃ has also been used. Commercial 3 mm pellets of γ -Al₂O₃ (414069 SIGMA–ALDRICH) have been crashed and sieved

to have a 300 μ m < dp < 500 μ m support material. The oxygen carrier has been prepared according to the procedure described in Cabello et al. [55], by impregnating the support material with saturated iron nitrate solution [Fe(NO₃)₃·9H₂O 3.5 M] at ambient temperature and calcined for 6 h at 1000 °C. The resulting OC corresponding to 20%wt. Fe₂O₃ was tested in TGA to study the reactivity in the presence of different syngas (CO/H₂/CH₄).

The results presented in Fig. 5 show that the reduction of Fe₂O₃ with CH₄ is very slow and the particle is not reduced further than Fe₃O₄ (blue line). The same trend is observed also in case H₂/CO₂ ratio equal to 1 and it slowly increases when this ratio is higher than 2. When H₂ (or CO) are fed to the system, the presence of methane does not affect the solid conversion. When H₂ and CO are used the mass change is limited to 1.9% which correspond to the reduction of Fe₂O₃ to FeO. If only Fe species are considered, the reduction should continue to pure Fe, however, in presence of Al₂O₃, a spinel FeAl₂O₄ (hercynite, formally FeO + Al₂O₃) is formed. The same results have been presented in Kidambi et al. [56] and confirmed by the chemical equilibrium accounting for the presence of alumina and iron-aluminate. These results have been confirmed also from the X-ray diffraction analysis of the oxygen carriers after the reduction with syngas containing H₂ and CO at 850 °C (Fig. 6).

2.2. Reactor design

Different reactor designs can be adopted for the PCCL process. Dynamically operated packed bed reactors have been selected here in view of the high pressure operation, which is required to achieve a high overall energy efficiency. Compared to the CLC technology with packed bed reactors, the PCCL concept does not require chal-

Fig. 5. Reduction of Fe_2O_3 (20wt.) supported with Al_2O_3 using different syngas compositions.

Fig. 6. X-ray diffraction (XRD) images of fresh OC (figure a) and reduced (figure b) with H_2 (20% diluted with N_2) at 850 °C in the TGA experiment.

lenging components such as HT-switching valves and piping because the process works at much lower temperatures (600–900 °C). Moreover, the PCCL system is less demanding (reducing the footprint of the plant) because of the lower overall heat of reactions¹; in fact, the heat removal phase in the packed-bed CLC technology, which requires by far the largest number of reactors to be operated in parallel as discussed by the authors in [57], is marginal or even not required

The reactor design strongly depends on the properties of the selected oxygen carrier and influences the required operating temperature to achieve high conversion, the gas composition to avoid carbon formation or chemical and thermo-mechanic problems, such as sintering or agglomeration.

In Fig. 7, different possible reactor configurations are considered: (a) the single stage adiabatic reactor, which is the basic PBR configuration; (b) the multistage adiabatic reactor, in which two (or more) different oxygen carriers can be used in series as discussed for packed-bed CLC by Hamers et al. [29]; (c) the single (or multistage) cooled reactor in order to keep the outlet gas temperature low. Although the selection of the optimal reactor configuration and best heat management strategy should go hand-in-hand with the optimization of the OC, it can already be pointed out that the PCCL concept shows a higher flexibility

in the reactor design increasing the feasibility of the technology when compared with CLC. The packed bed heat management and temperature control can be carried out by selecting a proper oxygen carrier composition and avoid locally excessive temperature increase and material thermal stress: working at lower temperature, as required in the PCCL concept in comparison with CLC, reduces the cost of design HP reactor vessels and, on the other hand, decreases the demand on the thermos-stability of the OC. Another aspect which is worth mentioning is the pressure drop effect on the process efficiency: the integration of packed-bed CLC with a combined cycle is strongly influenced by the pressure drop over the CLC-reactors, since it influences the power consumption for air compression for the air during the oxidation (and heat removal) phase. In the PCCL concept the gas turbine has to bring the air stream to the oxidation reactor to a higher pressure in comparison to conventional NGCC, which may lead to some efficiency penalty. However, this is less disadvantageous when compared with a CLC plant, where all the gas from compressor is sent to the CLC reactors, which renders the two parts of the plant mutually dependent, especially concerning the selection of the operating pressure and temperature.

3. Experimental results

Breakthrough experiments have been carried out using a μPBR (Fig. 8) filled with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and placed in a furnace. The reaction temperature was controlled by K-type thermocouple which has been inserted inside the μPBR . The furnace is filled with sand which is fluidized in order to keep the temperature of the system

¹ In CLC the overall heat of combustion released to convert CH_4 into H_2O and CO_2 is $-802.3 \text{ MJ/kmol}_{\text{CH}_4}$ while in case of PCCL the overall heat of reaction to produce H_2O and CO_2 and a gas mixture of H_2/N_2 (50%/50% on molar basis) is $-157.8 \text{ MJ/kmol}_{\text{CH}_4}$ and increases to $-250 \text{ MJ/kmol}_{\text{CH}_4}$ in case of H_2/N_2 (40%/60% on molar basis) due to the larger amount of air required to increase the N_2 content in the H_2 -rich gas.

Fig. 7. Reactor design: (a) single stage adiabatic configuration, (b) multi-stage adiabatic configuration; (c) single stage reactor integrated with heat exchanger.

Fig. 8. Micro-packed bed reactor used for the iso-thermal breakthrough experiments.

uniform and isothermal. The gasses at the outlet of the reactor have been cooled down and after water separation the remaining gasses have been analyzed with a mass spectrometer coupled with a CO analyzer.

A sequence of reduction and combined steam–air oxidation has been carried out using different inlet fuel compositions based on $\text{CO}/\text{H}_2/\text{CH}_4$ gases diluted with CO_2 . The results of the selected experiments are presented in Fig. 9.

- (1) In case a mixture of $\text{CO}/\text{H}_2/\text{CO}_2$ is used (Fig. 9a,b reduction), the bed is reduced to a mixture of FeO (intended as FeAl_2O_4) and Fe_3O_4 . After the breakthrough, the syngas composition does not reach the same inlet composition due to the catalytic properties of FeO for the reverse WGS reaction.
- (2) Due to the resulting oxygen carrier composition after reduction cycle in Fig. 9a–c, it is possible to observe the production of the H_2 at the beginning of the corresponding oxidation cycle which increases by increasing the $(\text{CO} + \text{H}_2)/\text{CO}_2$ ratio during the reduction.
- (3) When using CH_4 and CO_2 (CH_4/CO_2 molar ratio equal to 1) at 850°C as in the reduction in Fig. 9c and d the conversion of CH_4 is almost completed. During the reduction time, only CO_2 is detected and the CH_4 concentration decreases; after the oxygen carriers is completely reduced to FeAl_2O_4 the H_2 and CO reach the breakthrough and no CH_4 appears: this

behavior can be explained by the catalytic activity of the reduced oxygen carrier for the methane reforming. The resulting H_2/CO ratio is about 1.1 which is very close to the equilibrium composition (H_2/CO ratio equal to 1) and the differences is explained by the presence of some CO_2 in the products (due to the WGS activity of the material as explained before). Carbon deposition does not occur at these conditions and this is confirmed also by the oxidation where no CO_2 is detected except for the small amount already present in the air. The positive effect of dry reforming in the OC reduction cannot be predicted in the TGA experiments because the gas flow rate is very high in order to have (almost) constant gas composition (and therefore the CH_4 is very small).

- (4) The reduction of Fe_2O_3 using CH_4 as fuel strongly depends on the operating temperature: when working at 750°C (Fig. 9e) the CH_4 breakthrough occurs almost immediately and the OC is not converted. However, in case an equivalent composition ($\text{H}_2 + \text{CO}$) is used as reducing gas the reduction of Fe_2O_3 occurs without unexpected fuel slip. Therefore, when working at lower temperatures, the oxygen carrier needs to be more active for methane reforming (e.g. by adding some Ni or other metals which are commonly used as reforming catalyst and as oxygen carrier for chemical looping reforming, see a.o. Medrano et al. [58]).
- (5) The resulting composition at the oxidation stage shows that the longer is the reduction time the higher is the amount of H_2 that can be obtained during the oxidation. When the oxidation is carried out with a small amount of air (25 ml/min) and higher amount of H_2O (60 ml/min) compared to the cases in Fig. 9a–c the reaction front of the steam-oxidation is faster than the reaction front of the O_2 . However, in case a similar number of moles of atomic oxygen from Air and H_2O are fed to the system (Fig. 9d), the amount of H_2 produced does not change significantly and the O_2 breakthrough is faster.

Preliminary experimental tests have been carried out in a packed-bed reactor that has been built and used for CLC [45,46] over the past years. The focus of these experiments is not on the reduction cycle, which is obviously also essential for a successful implementation of this technology, but this cycle does not differ from conventional packed-bed CLC systems.

The experimental study here is focused on providing a first proof-of-principle of the PCCL concept, whose novelty lies in the oxidation cycle.

3.1. Description

The experimental setup consists of a high temperature stainless steel tube ($\text{OD} \times \text{ID} \times \text{L} = 35 \times 30 \times 1500 \text{ mm}$) that contains oxygen carrier particles. The reactor is heated by three ovens with a capacity of 200 W (insulated with KVS125) per oven, which have been installed around the reactor tube. The reactor and oven have been insulated using vermiculite. The temperature of the bed is set using three thermocouples located inside the oven which control the power supplied to the system, while the temperature of the bed is measured with 48 thermocouples (Rössel, type K) which are installed inside the reactor and in direct contact with the particle.

A simplified scheme of the setup is depicted in Fig. 10.

The feed flow rate and composition is controlled by Bronkhorst mass flow controllers. The outlet stream of the reactor is cooled down with a water cooler and the produced water is collected and separated. The pressure is controlled by a back pressure controller (Bronkhorst). The dry composition is measured with a mass spectrometer (MKS Cirrus 2 using an additional IR-analyzer for CO to distinguish the CO and N_2 by the mass spectrometer).

Fig. 9. Iso-thermal breakthrough tests of reduction, and PCCL oxidation.

Fig. 10. Simplified schematic overview of the packed bed reactor setup [59,61].

Fig. 11. Syngas ($\text{H}_2/\text{N}_2/\text{O}_2$) composition at the reactor outlet during the oxidation (feed gas 20 L/min 0.55 H_2O and 0.45 air on a molar basis) for different operating temperatures.

3.2. Analysis

Due to the large amount of particles required, alumina-supported hematite could not be used for these test. The experiments have been carried out by using 530 g of oxygen carrier (25% of Fe_2O_3 and 75% clay on wt. basis) distributed in 50 cm of reactor length. The experiments are focused on the oxidation cycle that is carried out 20 L/min of a gas mixture of air and steam (0.55 and 0.45 of H_2O and air respectively on mole basis) at ambient pressure and temperature in the range of 600–800 °C. The reduction has been carried out using 6.5 L/min of diluted H_2 ($\text{H}_2/\text{H}_2\text{O}/\text{N}_2$: 0.15/0.15/0.7) for 1 h in order to reduce the Fe_2O_3 to FeO at 800 °C. After the reduction cycle, the reactor has been purged for at least 20 min with N_2 in order to completely purge the syngas left after the reduction cycle. In order to reach the desired temperature of the reactor, the setpoint of the reactor has been changed and the bed cooling has been carried out by flowing N_2 inside the reactor.

The purpose of these experiments is to study the thermal behavior of the bed in the presence of the reactions considered in the system and to perform a lab-scale analysis using a bigger reactor system in which it is possible to have longer redox cycles than the previous experiments carried out with the reactor depicted in Fig. 8. Moreover, due to the reactor system used, it is possible to see the bed temperature profile during the oxidation step.

When the solid has reached the reaction temperature the oxidant stream is fed to the reactor for more than 1 h until the gas composition at the reactor outlet was constant and the solid has been completely oxidized. The composition of the gas exiting the reactor during the oxidation cycle for different temperatures during the oxidation is shown in Fig. 11. Four different experiments have been carried out: in the first three cases the initial active com-

ponent in the OC was FeO at different operating temperatures (from 600 to 800 °C); in the fourth case, the initial active component in the OC was Fe, where the complete reduction of the OC to Fe was obtained with a H_2/N_2 mixture at 700 °C (in this case the composition fed was H_2/N_2 : 0.2/0.8 for 1 h).

The mole fraction of the produced H_2 is in the range of 5–8% on wet basis for the cases of oxidation from FeO to Fe_2O_3 . The H_2 concentration increases during the cycle until a maximum concentration is reached after which it starts to decrease. When the bed is almost completely oxidized, also the O_2 breakthrough is detected (after about 2000 s). Due to the relatively slow kinetics of the OC used, the H_2 production is not constant and the conversion is lower than the conversion at thermodynamic equilibrium. At the equilibrium conditions,² (see Fig. 12), the H_2 molar fraction is in the range of 20–40% for the temperature range of 600–800 °C. For the case when the OC was fully reduced to Fe before the oxidation cycle started, the H_2 content is 12.5% closer to its equilibrium value of 35% (on a wet basis), the H_2 breakthrough is steeper and more H_2 is produced compared to the previous cases. The fluctuations on the H_2 concentration could be related to the variations in the pump used for the water feeding to the system as well as the effect of gas diffusion in the components downstream the reactor due to the high volume of the gas cooler and piping to the gas analyzer.

Increasing the initial solid temperature, the amount of H_2 produced at the reactor outlet increases due to the faster kinetics of H_2O -splitting, however, the final composition never reaches the equilibrium composition. Another important aspect is the temperature rise that occurs in the reactor during the oxidation cycle. In

² For the equilibrium calculation only Fe_2O_3 , Fe_3O_4 , FeO and Fe have been considered as possible solid phases. the calculation is carried out using the software HSC which calculates the final species compositions by minimizing the Gibbs free energy.

Fig. 12. Calculated gas composition after oxidation using Air/H₂O 45%/55% when assuming chemical equilibrium for the cases starting with FeO (or Fe) as OC at 600 °C, 700 °C and 800 °C. The chemical equilibrium has been calculated by assuming a system with large amount of FeO (or Fe) and feeding a small amount of gas and check the gas composition at the selected temperature.

Fig. 13. Temperature profile during the oxidation cycle for different initial bed temperatures: (a) 600 °C; (b) 700 °C; (c) 800 °C. Each curve represents the temporal evolution of the bed temperature at different axial positions along the reactor (indicated in figure d), starting with FeO as reduced oxygen carrier.

Fig. 13, the temperature profile at different axial positions inside the reactor is shown. It can be seen that the temperature rise is in the range of 100–130 °C and it increases with decreasing initial bed temperature. The decrease in the temperature rise at higher initial bed temperatures is mainly related to the increase in the heat losses in the lab-scale set-up, where heat losses play an important role in the thermal energy balance. For all the cases, the maximum temperature rise does not occur at the beginning of the reactor (tc_1 curve), but in the central part of the reactor (tc_2 and tc_3), because of the higher bed temperature when the reac-

tion front reaches these points: the solid is continuously heated by the high temperature gas that has already reacted and therefore the reaction start with a higher solid temperature. The thermocouple tc_5 is located at the end of the reactor and the temperature rise when the reaction front is passing is almost zero: in this case, the heat of reaction and the heat transfer is almost completely compensated by the heat losses in the system. From the results shown in Fig. 13 it can be concluded that in these experiments, the reaction front is slow and thus the reaction and heat front velocities have the same order of magnitude. These experimental results

Fig. 14. Comparison between the fresh (case a) and used (case b) OC material: microscopic picture (case 1) and SEM image (case 2).

Fig. 15. EDX analysis of the fresh (case a) and used (case b) OC material.

have been compared also with CLC (i.e. feeding undiluted air) and steam-iron (i.e. feeding pure steam) processes. In case of CLC, using the same oxygen carrier and the same solid composition (from FeO to Fe₂O₃) the maximum temperature rise achieved in the reactor is higher than 500 °C (not shown in this paper). For the steam-iron process, the oxidation is divided in two consecutive steps. In the first step, H₂O is fed to the reactor and FeO is converted into Fe₃O₄. In this step the temperature hardly changed due to the small heat of reaction and the slow redox kinetics. In the second step the solid is completely oxidized to Fe₂O₃ with air and the maximum temperature rise measured was 50 °C. These results confirm that the expected temperature rise of the PCCL concept is in between the CLC and steam-iron processes. This conclusion is also confirmed by the theoretical temperature rise presented by Noorman et al. [62] and discussed from numerical and experimental point of view in other works [27,29,63].

Photographs and SEM images of the fresh solid OC material and the materials after the tests in the packed bed reactor are shown in Fig. 14. It can be seen that the OC has changed after repeated cycles under reacting conditions and at different temperatures. The SEM images show that the fresh material (Fig. 14a) is less heterogeneous and the surface area is higher than for the used material (Fig. 14b) which shows a more uniform surface. From the images, it is also possible to discern some effect of agglomeration, which often occurs with Fe-based oxygen carriers especially when unsupported [45,64]. Another change in the material surface is also indi-

cated from the energy dispersive X-ray analysis (EDX) shown in Fig. 15, which shows that the presence of Ca, Si, Al components was not detected for the used OC material. This may indicate that there has been a migration of the iron to the external surface. This iron migration has also been found by others [54,65,66].

From this analysis and the results obtained from the experiments on the reactor behavior, three main conclusions can be drawn: (i) the material is not optimized, and the use of supported oxygen carriers may be beneficial to achieve a sustained increase in the surface area; (ii) a decrease in the agglomeration and an improvement in the thermal stability of the material is required; (iii) the operating temperature affects the kinetics of the oxidation reactions and therefore the heat management of the reactors must be properly arranged. On the other hand, the initial bed temperature does not affect the temperature rise as a result of the exothermic reactions between the oxygen carrier and the steam/air gas mixture.

4. Concept and integration

4.1. Plant description

In order to investigate the potential of the PCCL system for power production, a preliminary assessment of the integrated plant and its comparison with the state-of-the-art technology for

Fig. 16. NG power plant integrated with the PCCL process.

natural gas fuelled combined cycle with and without CO₂ capture have been carried out and is reported in this section. The plant layout is shown in Fig. 16. After the hydro-desulfurization unit (in which the H₂S content is reduced to below 100 ppb), required to avoid catalyst poisoning, the sulfur-free natural gas is first mixed with steam and then with recirculated exhaust gas to reach a proper S/C ratio to avoid carbon deposition and enhance the conversion of methane and higher hydrocarbons (stream #10). After pre-heating the mixed syngas up to 500 °C, the syngas is sent to an adiabatic pre-reforming unit (#11), in which all the C₂₊ components are converted into CH₄ and some H₂/CO is produced. Syngas fuel (#12) is first pre-heated at 600 °C using the high temperature CO₂-rich stream (#14) and later fed to the packed bed reactor(s) operated in reduction. In the fuel reactor the complete conversion of the syngas with the oxygen carrier(s) takes place and the resulting CO₂-rich stream is delivered from the reactor at around 750–800 °C (#13). The exhausts are cooled down and part of the exhaust gases (#14) are recirculated back to reduce the risk of car-

bon deposition. In this analysis, two different configurations are considered: in the first case (here referred as PCCL-HP), the exhausts are kept at the operating pressure and cooled down by producing HP superheated steam (#29). In order to enhance the steam turbine power output, a LP steam generator is also included and after that (#26), the steam is condensed and the pure CO₂ stream at high pressure is sent to the final stage of compression for long term storage (#16). In the second case (PCCL-LP), the exhaust gasses are first expanded to 5 bar and the gasses are cooled by pre-heating high pressure water, which is used in the HRSG. After H₂O is condensed, the CO₂ is compressed up to 110 bar.

From the other side of the plant, the air (#1) is fed to a gas-turbine compressor and compressed up to 17 bar. Part of the air is fed to a booster compressor which increases the air pressure up to the PCCL pressure. Air is then mixed with steam from the steam cycle and sent to the PCCL reactor(s) in oxidation (#3). At the reactor outlet, a gas mixture of H₂/N₂/H₂O with some traces

of Ar and CO₂ is produced and cooled down to 500 °C (#4). A small part of the H₂-rich gas is cooled to ambient temperature and sent to the hydro-desulphurization beds (#17). The main portion of the H₂/N₂/H₂O mixture is sent to the gas turbine combustor (#5). The exhaust gasses (#6) are expanded in a cooled gas turbine and cooled in a heat recovery steam generator (HRSG) with two or three pressure levels depending on the process requirements.

It is worth noting that, qualitatively, in case the PCCL concept is applied to an ammonia production unit, the plant design would not change significantly: from the fuel side the main difference is related to the required thermal integration, while from the H₂/N₂ side the power island is significantly simplified and the main stream of produced H₂/N₂ is sent to the compressors train and to the ammonia synthesis unit.³

4.2. Assumptions and methodology

Simulations have been carried out by the proprietary computer code GS [67] developed by the GECOS group at the Energy Department of Politecnico di Milano. The simulation code is designed according to a modular structure allowing to calculate complex plant configurations. Among the components available in the code (e.g. compressor, expander, splitter, mixer, heat exchanger, combustor, pump), the gas turbine model deserves particular attention, because it is able to simulate a cooled expansion on the basis of a one-dimensional design of the turbine stages for an accurate estimation of the cooling flows for each row as described in [68]. Since this model is based on general correlations whose validity is independent of the working fluid properties, it can effectively predict the behavior of the H₂-fuelled gas turbine included in the plants considered in this study [69]. The CO₂ compression unit is calculated using Aspen Plus 7.3 (Aspen Technology, 2011), adopting the Peng–Robinson equation of state with default coefficients for the evaluation of the fluid mixture properties. The main assumptions are taken from the EBTF document and properly adapted according to the design of the plant [10] (see Table 2).

Although PBRs are dynamically operated and thus the gas conditions at the reactor outlet vary in time depending on the heat management and system design, in this analysis we assumed a constant temperature and concentration corresponding to the time-averaged situation, mimicking the case where several reactors are operated in parallel out-of-phase and produce the gaseous streams at different conditions and are then mixed, as amply discussed by the authors in [57]. This assumption must be verified with the support of more advanced reactor models. We can already anticipate that in the PCCL concept high temperature gas (around 1200 °C as for the CLC) for the gas turbine is not required and therefore the expected temperature change inside the reactor will be much less pronounced.

The amount of excess H₂O during the oxidation cycle depends on the OC formulation and cannot be exactly estimated here. For the base case, a H₂O excess of 50% has been assumed (with respect to the stoichiometric amount required) based on equilibrium calculations for Fe and FeO as reduced OC at different temperatures (see Fig. 17). It must be noticed that the operating point selected for the plant analysis represents an intermediate condition (a mixture of Fe and FeO at the equilibrium condition). As previously mentioned, the OC design and engineering for this specific process has not been carried out yet and therefore we have limited our analysis to a single case before the modeling and design of the reactor for the process will be studied more in detail.

4.3. Analysis of the results

The thermodynamic conditions of the main streams represented in Fig. 16 are shown in Table 3. The mass balance refers to the optimized plant layout of the PCCL-HP system. The syngas fed to the reactor operated in reduction (#12) is highly diluted (S/C = 2.2 and CO₂/C = 0.86) in order to increase the CH₄ conversion which may also take place through SMR and WGS, when the OC has a catalytic activity for these reactions. The syngas composition should be carefully selected in order to achieve the proper conversion of the OC (e.g. from Fe₂O₃ to Fe/FeO) and avoid carbon deposition which is favored by the operating temperature (600–900 °C) and the high pressure. However, based on conventional industrial applications for steam and dry methane reforming H₂O(+CO₂)/CH₄, the current ratio is enough to avoid the risk of carbon formation, whether some Ni is added in the bed to promote the reforming reaction (from 2.5 to 5 [70,71]). At the oxidation side, the amount of steam used for the process is 88.5 kg/s (#18) and only 66% of the molar flow rate is converted into H₂, while the entire amount of O₂ from air is used for the oxidation reaction. The resulting syngas composition (#5) does not need any additional dilution to limit the NO_x since the stoichiometric flame temperature of 2168 K is expected to be sufficiently low to limit NO_x formation. After the CO₂ process unit (CPU), the CO₂ purity is higher than 97%: the remaining gas is N₂ which comes from the H₂-rich gas for the desulphurization beds. In order to increase the purity up to 99% a small PSA unit could be used to purify the H₂ to the natural gas treating: the efficiency of the system would only be slightly affected (–0.3 percentage points) and only a small PSA unit is required to treat 5600 Nm³/h gas and separate about 1900 Nm³/h of H₂ in comparison to a conventional H₂ plant [72] (300'000 Nm³/h) with no relevant effects in the plant economics. From the steam cycle integration it is possible to notice that more than 60% of the gas expanded in the steam turbine is later used for the process (at 26 bar) (stream #18 + #19). For the PCCL-HP, the LT heat recovery will provide some additional steam (#26) at 4 bar, which will be beneficial for the steam turbine power output.

Table 4 shows the comparison among the novel plants and two benchmark natural gas plants. The NGCC is the conventional combined cycle that represents the best available technology for power production using natural gas as fuel. The second benchmark technology is a natural gas combined cycle with post-combustion capture via chemical absorption using mono-ethanolamine (MEA) solvent. The performance of the conventional plants have been taken from the EBTF report [10] and slightly adapted.

The post-combustion CO₂ capture (NGCC-MEA) shows an efficiency loss of 8.5 percentage points which are mostly concentrated in a lower steam turbine power production due to the amount of steam required for the MEA reboiler (–5.5%) and the rest is due to the compression of CO₂ (–1.5%) and of the HRSG exhausts before the absorption unit (–1.05%).

The PCCL plants show an electrical efficiency between 49% and 50.8% depending on the configuration. The efficiency losses are comparable with NGCC + MEA. In terms of CCR, the PCCL system would be able to capture virtually 100% of CO₂ as typically achieved in all the chemical looping systems. In terms of specific primary energy consumption for CO₂ avoided (SPECCA⁴) the PCCL-HP system performs about 17% better due to the lower CO₂ specific emissions. The comparison between the benchmark technology with CO₂ capture and the PCCL systems shows that, despite the gas turbine power production is higher for the NGCC + MEA

³ In case of NH₃ production, CO₂ is coming from the air. It must be verified if the resulting amount of CO₂ in the H₂/N₂ stream (which would be around 125 ppm) is not too high for the catalyst in the NH₃ synthesis unit.

⁴ $SPECCA = \frac{\left(\frac{\eta_{ref}}{E_{CO2,ref}} - \frac{\eta}{E_{CO2}}\right)}{\left(\frac{\eta_{ref}}{E_{CO2,ref}} - \frac{\eta}{E_{CO2}}\right)} \times 3600$ where η and E_{CO2} are respectively the electrical efficiency and the specific CO₂ emissions of the reference plant (NGCC) and the considered plant.

Table 2

Main assumptions used for the thermodynamic analysis.

Combined cycle main assumptions			
Gas turbine		Heat recovery steam generator	
Compressor pressure ratio	16.9	HRSG gas side pressure loss, kPa	3
Compressor polytropic efficiency, %	92.5	Heat losses, % of heat transferred	0.7
Turbine polytr. eff. cooled/uncooled stages a, %	93.3/93.5	Subcooling/pinch/min. approach points, °C	5/10/25
Organic efficiency, %	99.865	Pressure level, bar	144/variable/4
Mechanical efficiency of compressor/turbine, %	99.6	Maximum steam temperature, °C	565
Electric generator efficiency, %	98.5	Pressure losses in HP /LP economizers, %	25
Turbine Inlet Temperature, °C	1360	Pressure losses in superheaters, %	7
Steam cycle		Heat exchangers	
Condensing pressure, bar	0.048	IP steam turbine polytropic efficiency, %	94
Power for heat rejection, MJ _e /MJ _{th}	0.01	LP steam turbine polytropic efficiency, %	92
Pumps adiabatic efficiency, %	70	Turbine mechanical efficiency, %	99.6
HP steam turbine polytropic efficiency, %	88	Electric generator efficiency, %	98.5
CO ₂ process unit		Heat exchangers	
IC compressor isentropic efficiency, %	84	Minimum ΔT in liquid-liquid, °C	10
IC compressor mechanical efficiency, %	94	Minimum ΔT in gas-liquid, °C	10
Last stage IC compressor CO ₂ discharge pressure, bar	89.1	Minimum ΔT in gas-gas, °C	25
Pump mechanical efficiency, %	94	Minimum ΔT in condensing-liquid, °C	3
Pump hydraulic efficiency, %	80	Heat losses, % of heat transferred	0.7
CO ₂ purity, %	>96%	Pressure drop liquid phase, bar	0.4
CO ₂ delivery pressure, bar	110	Pressure drop gas phase, %	2
CO ₂ delivery temperature, °C	35	Maximum steam T in the Syngas Coolers, °C	400

(355.6 MW_e vs 319.6 MW_e), the steam cycle performance compensates the power production gap (this is true for the PCCL-HP) and the other differences are due to the cost of H₂/N₂ production (PCCL system) and CO₂ compression (NGCC + MEA).

A comparison between the PCCL-HP and PCCL-LP configurations shows that the system in which the CO₂-rich stream from the reactor in reduction is directly cooled down producing HP steam is more efficient than the system with an exhaust expander. The comparison can be summarized in the following points:

- The gas turbine production is the same, but the steam cycle performance is different because more steam is produced during the exhaust gas cooling (PCCL-HP). In the PCCL-HP, the possibility to produce LP steam would improve significantly the performance of the system (the increase in the steam turbine power output due to additional LP steam is about 23 MW_e). The beneficial recovery at low temperature is not possible for the PCCL-LP, because there is not enough heat available to produce LP steam.
- The presence of the exhaust expander in the PCCL-LP increases the power output with 30 MW_e and at the same time the CO₂ compression consumption increases with 5.22 MW_e.
- The CO₂/H₂O expander is not a conventional component, the heat exchangers for LT heat recovery would require larger volumes due to the lower pressure of the gasses and the CO₂ compression unit will require more stages.

A sensitivity analysis has been carried out on the amount of steam required in the PCCL process for the PCCL-HP configuration. Decreasing the amount of steam from 88.5 kg/s (as for the mass balance reported in Table 3) to 64.9 kg/s, the H₂ molar fraction of the syngas at the combustor increases to 52.14% (with respect to 43.1%) and the STF increases to 2348 K (about 50 K higher than the selected limit for NO_x control). However, the electrical efficiency of the plant significantly increases from the current 50.8% to 51.9% mostly because the steam turbine power output increases by 20.1 MW_e due to the lower amount of steam consumed in the process. The possibility to use less steam for the oxidation process must be verified also accordingly to the OC performance as discussed before.

5. Conclusions

A novel concept that combines chemical looping technologies and pre-combustion CO₂ capture has been presented, multiple experimental analyses at the material and reactor level have been investigated and discussed in this paper. The thermodynamic and experimental analyses have shown that in presence of an Fe-based OC, the oxidation step in a packed bed reactor can be achieved with a gas mixture of H₂O and air that are converted into H₂/N₂ (and unreacted H₂O) in the temperature range of 600–900 °C. Also in presence of CH₄, the fuel conversion is complete and the reduced OC is suitable to produce a combined mixture of H₂ and N₂ during the PCCL oxidation. In presence of pure Fe₂O₃ to FeO/Fe the H₂ production is significantly lower (also compared to the equilibrium conditions), indicating that further optimization of the oxygen carrier is necessary to achieve high gas conversion especially for the H₂O splitting reaction that is not as fast as the OC oxidation with air. The analysis of different formulations of OC is required in future works in order to select the most promising material(s) for the process. Additionally, the importance of the kinetic and mass transfer limitations on the overall efficiency need to be assessed in more details once a better OC has been identified for this reaction system. Beside the technology formulation and proof of principle which has been presented in the experimental analysis, a thermodynamic analysis has been carried out to assess the expected performance that can be achieved for the electricity production with CO₂ capture. From a process integration point of view, the process here presented appears promising because it allows to convert the fuel into a concentrated H₂/N₂ gas mixture by reducing the number of conversion/separation steps and does not require very high temperature reactors (as well as valves, piping, etc.) as in chemical looping combustion systems, where this represents a technological and economic challenge. The thermodynamic assessment of the integrated system and the comparison with benchmark technologies confirmed the potential of the PCCL systems in terms of expected electrical efficiency and CO₂ capture rate. According to the analysis, it can be concluded that a proper thermal integration is very important for the overall performance and the use of a CO₂/H₂O expander is not beneficial for the effi-

Fig. 17. H₂ and H₂O gas fraction at the thermodynamic equilibrium using a Fe or FeO as reduced OC and a mixture of 60% H₂O, 31.5% of N₂ and 8.5 of O₂ for the oxidation stage.

Table 3

Thermodynamic conditions of the selected point (#) in Fig. 12.

	T	P	m	MW	Q	Stream composition (vol. basis)											HHV	LHV
	°C	bar	kg/s	kg/kmol	kmol/s	Ar	CH ₄	C ₂₊	CO	CO ₂	H ₂	H ₂ O(g)	H ₂ S	N ₂	O ₂	H ₂ O(l)	MJ/kg	MJ/kg
#1	15.0	1.01	669.7	28.9	23.21	0.9				0.0		1.0		77.3	20.7			
#2	403.9	16.95	491.4	28.9	17.03	0.9				0.0		1.0		77.3	20.7			
#3	490.0	25.74	186.2	22.4	8.30	0.4				0.0		59.6		31.5	8.5			
#4	777.0	24.22	110.6	14.7	7.53	0.4				0.0	43.1	21.8		34.8			9.0	7.1
#5	353.0	23.26	109.8	14.7	7.47	0.4				0.0	43.1	21.8		34.8			9.0	7.1
#6	1435.6	16.45	546.6	26.0	21.00	0.8				0.0		23.8		68.1	7.3			
#7	618.6	1.04	681.8	26.5	25.69	0.8				0.0		19.7		69.8	9.7			
#8	74.8	1.04	681.8	26.5	25.69	0.8				0.0		19.7		69.8	9.7			
#9	10.0	70.00	20.0	18.0	1.11		89.0	8.1		2.0			5 ppm	0.9			51.5	46.5
#10	394.2	26.01	30.6	17.9	1.71	0.0	57.9	5.3		1.3	1.4	32.5		1.7				
#11	500.0	25.49	105.6	22.8	4.63	0.0	21.3	1.9	0.0	18.8	0.5	56.3		1.0			35.3	31.1
#12	600.0	25.49	105.6	22.8	4.63	0.0	22.9		0.3	19.6	4.8	51.3		1.0			10.9	8.9
#13	800.0	24.22	181.1	25.6	7.06	0.0				29.1		70.2		0.7				
#14	390.0	22.79	75.0	25.6	2.92	0.0				29.1		70.2		0.7				
#15	117.4	21.02	106.1	25.6	4.14	0.0				29.1		2.9		0.7		67.3		
#16	26.8	110.00	53.3	43.9	1.21													
#17	35.0	1.04	5.8E-01	13.8	0.04	0.5				0.0	54.9	0.2		44.3			11.4	9.6
#18	500.0	26.01	88.5	18.0	4.92							100.0						
#19	500.0	26.01	10.0	18.0	0.56							100.0						
#20	32.1	0.05	106.9	18.0	5.93											100.0		
#21	338.9	144.00	77.1	18.0	4.28											100.0		
#22	16.8	190.00	19.6	18.0	1.09											100.0		
#23	338.8	144.00	58.6	18.0	3.26											100.0		
#24	562.0	133.90	165.3	18.0	9.19							100.0						
#25	564.2	23.92	66.8	18.0	3.71							100.0						
#26	172.7	4.00	39.0	18.0	2.17							100.0						

ciency of the plant. Moreover, the present system can be also adopted for ammonia production in which the use of a single process would significantly reduce the plant costs eliminating the need of several steps such as steam reforming, WGS and methanation reactors as well as a CO₂ absorption unit. The feasibility of the PCCL process, its integration and the techno-economic evaluation and comparison with conventional ammonia production plants will be carried in a future study. Nomenclature and abbreviations.

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Table 4

Performance comparison of the PCCL systems and the benchmark technologies.

Configuration name	Units	NGCC	NGCC	PCCL-HP	PCCL-LP
CO ₂ capture technology		N/A	MEA	Oxyfuel	Oxyfuel
CO ₂ pressure			Low	High	Low
<i>Gas turbine</i>					
GT compressor	MWe	−345.45	−345.45	−262.09	−262.09
GT expander	MWe	707.95	707.95	586.98	586.98
Org/El losses	MWe	−6.87	−6.87	−5.35	−5.35
Exhaust Expander	MWe				30.00
<i>Steam cycle</i>					
ST gross power	MWe	192.29	140.96	178.47	137.71
Pumps	MWe	−2.34	−2.22	−4.02	−3.62
<i>Others</i>					
Exhaust Fan ^a	MWe		−9.80	−3.38	−3.38
Air Compressor (only PCCL)	MWe			−10.38	−10.38
CO ₂ treating system					
CO ₂ compression	MWe		−14.77	−5.46	−10.68
CO ₂ -unit pumps	MWe		−3.04		
BOP	MWe			0.01	0.01
Heat rejection aux.	MWe	−2.44	−2.87	−2.33	−2.40
Overall Gross Power	MWe	547.93	496.60	498.01	457.26
Overall Net Power	MWe	543.15	463.90	472.42	456.77
NG thermal input	MW _{LHV}	929.65	929.65	929.65	929.65
Gross electric efficiency	%	58.9%	53.4%	53.6%	49.2%
Net electric efficiency	%	58.4%	49.9%	50.8%	49.1%
Cold gas efficiency	%			83.5%	83.5%
Carbon Capture Rate	%		91.2%	100%	100%
CO ₂ avoided	%		89.7%	100%	100%
CO ₂ specific emissions	kg _{CO2} /MWe _h	350.60	36.12	0.00	0.00
SPECCA	MJ _{LHV} /kg _{CO2}		3.35	2.63	3.32

^a In NGCC with MEA the fan is used before the absorption unit, in PCCL is the CO₂/H₂O recycle fan.

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