

Possible optimal configurations for the ZECOMIX high efficiency zero emission hydrogen and power plant

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Received 4 January 2007

Abstract

Coal use for electricity generation will continue growing in importance. In the present work the optimization of a high efficiency and zero emissions coal-fired plant, which produces both hydrogen and electricity, has been developed. The majority of this paper concerns an integration of gasification unit, which is characterized by coal hydrogasification and carbon dioxide (CO₂) separation, with a power island, where a high-hydrogen content syngas is burnt with pure oxygen stream. Another issue is the high temperature CO₂ desorption. Because of the elevated temperature heat supply, the regeneration process affects the overall performance of ZECOMIX plant. An advanced steam cycle characterized by a medium pressure steam compressor and expander has been considered for power generation. A preliminary study of different components leads to analyze possible routes for optimization of the whole plant. The plant equipped with a CO₂ capture unit could reach efficiency close to 50%. The simulations of a thermodynamic model were carried out using the software ChemCAD.

This study is a part of a larger research project, named ZECOMIX, led by ENEA (Italian Research Agency for New technologies, Energy and Environment), other partners being ANSALDO and different Italian Universities. It is aimed at analyzing an integrated hydrogen and power production plant.

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Keywords: Coal hydrogasification; CO₂ capture; Hydrogen

1. Introduction

Hydrogen production from fossil fuels and renewable energy sources is a priority for Italian medium and long-term energy R&D policy. Carbon dioxide (CO₂) capture and storage is one of the main R&D activities in the priority theme “New Technologies for Energy Generation and Management” in the framework of the Italian Public Research Plan.

In Italy, technologies for CO₂ capture and storage are considered a main topic to be studied and demonstrated, and represent a significant opportunity for industries. In order to promote and sustain R&D initiatives for CO₂ capture and storage, Italy has recently joined the Carbon Sequestration Leadership Forum together with 11 other Countries and the European Union. The construction of a

bench scale plant aimed at realizing a coal gasification test plant at the ENEA research center has been recently funded by Ministry of Research for developing gasification technologies to produce hydrogen from coal.

At the present state-of-the-art, there is a strong, world-wide awareness on the topic, and several research projects are in progress at different research centers. Current technologies adopted for CO₂ capture imply low temperature ranges with high efficiency losses in the whole energy conversion process. Nowadays efforts are invested in developing coal-fuelled plants. A possible route is offered by well-known integrated gasification combined cycle (IGCC). In such a power generation technology the coal boiler is replaced with a conventional gasifier where coal gasification process with a certain amount of energy takes place.

Moreover, a technology for CO₂ capture from coal syngas by means of a solid sorbent is expected to have a strong impact in mitigating climate changes. A good-looking

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Nomenclature

h	massic enthalpy (kJ/kg K)
n	molar flowrates (mol/s)
s	massic entropy (kJ/kg K)
T	temperature (°C)
w	mass flowrates (kg/s)
W	power (MW)
η	efficiency

Acronyms

ASU	air separation unit
AUX	auxiliary device
CAL	calciner
CCU	CO ₂ capture unit
CG	cold gas
CGI	coal gasification island
CI	calciner island
CMB	combustor of plant 1's HTT
CMB1	combustor of plant 2's HTT
CMB2	additional combustor in the "plant 2" power island
COMP	steam compressor
COND	condenser
CHE	chemical

CRB1	high temperature carbonator
CRB2	low temperature carbonator
CRBN	combustor of calciner
ELE	electrical
EXP	expander
GEN	electric generator
HPT	high pressure turbine
HRSG	heat recovery steam generator
HSG	hydrogasifier
HTT	high temperature turbine
INC	incondensable gases
LH	low heating
PP	power plant
PUMP	water pump
SCMR	syngas to coal mass ratio (kg/kg)
SMR	steam methane reforming
SPT	splitter
SYN	syngas
TSSEMR	thermal swing sorption enhanced methane reforming
WGS	water gas shift
ZEC	zero emission coal
ZECOMIX	zero emission coal mixed technology
ZECOTECH	zero emission coal technology using hydrogen

route represents the pre-combustion CO₂-capture by using the thermal swing sorption enhanced methane reforming (TSSEMR).

In such a system the CO₂ produced in methane reforming is captured by means of solid sorbent so that hydrogen yield is enhanced.

As solid material has become soaked with CO₂, it will be driven to the desorber reaction, where a process of sorbent thermal regeneration takes place in the range of 850–900 °C and atmospheric pressure by means hot gas.

The objective of this work is to propose a pioneering coal gasification process based on hydrogasification integrated with a CO₂ capture process to produce hydrogen as fuel in an innovative steam cycle power plant [17,18]. The novelty in the proposed process, named Zero Emission COal MIXed (ZECOMIX), is that, despite the conventional gasification process used in IGCC plants, the coal hydrogasification is an exothermic reaction and no energy input is needed to produce syngas. In addition, efforts have been made to integrate in the proposed plant a TSSEMR system.

In the ZECOMIX plant, such a system is composed by a CO₂ capture unit (CCU) and a calciner island (CI). In the former unit a CO₂ capture takes place by means of calcium oxide in the latter, instead, the regeneration of solid sorbent happens.

Moreover, different power plant configurations based on this process will be presented and compared.

2. ZECOMIX concept description

Different paths have been investigated to reduce carbon emissions: one of these concerns a development of new gasification technologies, able to capture the inherent carbon content of coal. The ZECOMIX project, conceived by ENEA in the framework of national hydrogen project, is aimed at studying an integrated process, which produces both hydrogen and electricity from coal with zero emissions and very high efficiency. The ZECOMIX technology concept combines the zero emission coal (ZEC) gasification technology, studied by Los Alamos National Laboratory and ZECA Corporation [2], and with the Zero Emission COmbustion TEchnology (ZECOTECH) using H₂ based on hydrogen-fuelled internal combustion turbine cycles proposed by different authors in the framework of the WE-NET research program and in other studies [1,11,12,19,20]. The key element is the integration of the gasification process, characterized by coal hydrogasification technology and CO₂ sequestration with the power island, where an oxy-combustion occurs.

The plant proposed can be broken into the following four sections:

- Coal gasification island;
- CO₂ capture unit;
- Calciner island;
- Power plant.

2.1. Coal gasification island

The coal gasification island is composed by a hydro-gasifier and a desulfurizer. In the former reactor the hydrogen reacts with the coal in order to produce methane. Thus, this reactor is characterized by the following chemical reaction:

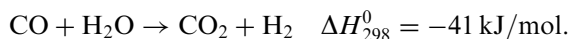
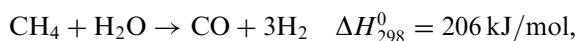


According to the kinetics of the process, pressure and temperature of the reactor have to be in the range of 30–60 bar and 700–800 °C.

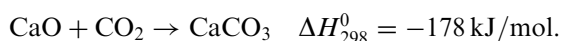
The latter reactor which composes the coal gasification island is a hot gas clean-up unit in which the desulphurization of raw syngas will be carried out by reacting any sulfur compounds (hydrogen sulfide, carbonyl sulfide) with a certain amount of calcium oxide based sorbent which is derived from the calcination island.

2.2. CO₂ capture unit

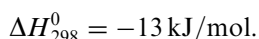
Carbon dioxide capture has been studied in previous works [10,13–15]. In CCU, a simultaneous process of CO₂ capture from coal syngas, and reforming of methane happens. The reforming of methane is based on two reactions, as



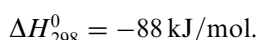
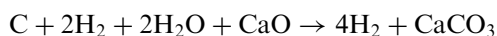
The former is an endothermic steam reforming reaction (SRR) and the latter is an exothermic water–gas shift (WGS) reaction. If an in situ CO₂ removal from the product gas mixture happens, the equilibrium limited reaction WGS moves forward. With this in mind, if the reforming reaction is carried out at the presence of a CO₂ adsorbant such as lime, the CO₂ capture reaction is



Therefore, energy demand of syngas decarbonization process can be estimated supposing the overall reaction in carbonators can be written as



The distribution of energy between the gasification island and CCU can be roughly estimated as



The process used in the hydrogen production is an exothermic one with a CO₂ removal, but despite traditional gasification process, in hydrogasification vessel energy input is not required.

Since the syngas shall be driven into the power plant, we will assume the operating pressure of CCU equal to that of

the combustion chamber in the power plant (30 bar) in order to avoid any syngas compressor. As a consequence, in order to permit the reforming of methane, CCU is envisioned as two carbonators working at two different temperature levels. The higher temperature carbonator supplies the hydrogen and water needed for the hydro-gasification. In the lower temperature carbonator, the uptake of CO₂ from the reaction zone will drive the equilibrium-controlled reactions forward.

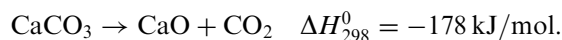
As a result, high conversion of CH₄, CO and H₂O in the lower temperature carbonator takes place at a temperature lower than conventional reforming temperature. Efforts have been made to evaluate the feasibility of the described advanced process finalized to the production of hydrogen and power from coal [3–5].

The only energy demanding section of the ZECOMIX process as a whole is CI.

2.3. Calciner island

When the solid material has become soaked with CO₂, it will be driven to a calciner, where a thermal regeneration process of the sorbent takes place.

The main purpose of this island is to regenerate CaO. The major chemical reaction is



Even though the gasification island does not need an energy input, it is requested in the calciner unit. An essential aspect of the whole process is the way by which the calcination process is carried out. As a consequence, this issue will receive the most intense level of discussion in the remainder of this paper.

2.4. Description of ZECOTECH cycle

The power island is based on an innovative steam cycle (ZECOTECH). This is a sort of combined cycle that uses steam as a working fluid, in both the topping and bottoming section. Fig. 1 illustrates the thermodynamic cycle in the temperature-entropy diagram and Fig. 2b shows the flowsheet of plant making real such a cycle.

2.4.1. The topping cycle

The topping cycle is composed by the following thermodynamic transformations (see Fig. 1): 0–2, 2–3, 3–4 and 4–1. Let us analyze in details the above-mentioned transformations. Firstly, a combustion process takes place in a combustor (CMB) at constant pressure (0–2). The flue gas, mainly composed by water steam, flows through a high temperature steam turbine (HTT) where an adiabatic expansion (2–3) takes place. The high temperature steam leaving HTT is then cooled (3–4) in a heat recovery steam generator (HRSG) producing secondary steam. The water steam leaving HRSG (point 4 in Fig. 1) is then divided into two streams. One of these streams is compressed by means of COMP through (4–1). The other one will be discussed in

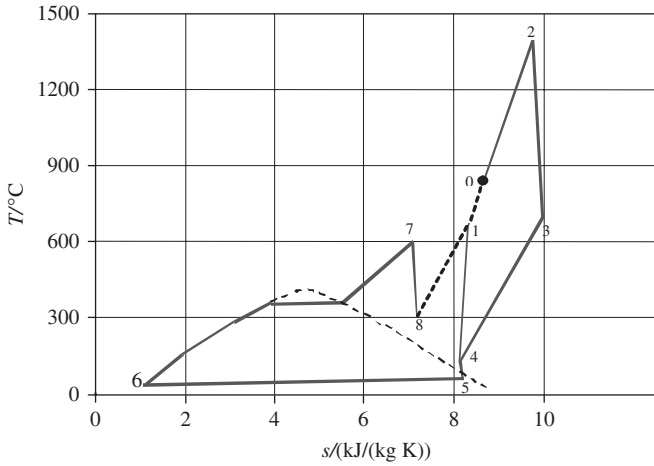


Fig. 1. ZECHOTECH cycle T - S diagram.

Section 2.4.2. The steam stream leaving the compressor (point 1) is injected into the combustion chamber and mixed with another certain amount of steam (i.e. the water steam (8), see later in Section 2.4.2.) reaching the point (0) of cycle and completing the topping section. The injecting of vapor in combustion chamber is necessary to prevent the combustion temperature from reaching value greater than 1400°C . Moreover, the dashed line (0–1) represents the irreversible mixing process involving the steam water (1) and (8). The topping section is a Brayton cycle using high temperature steam as working fluid, and its main parameters (temperature and pressure) have been chosen to accomplish the current turbo-gas using state of the art of gas turbine plants.

2.4.2. The bottoming cycle

The bottoming cycle is composed by the following thermodynamic transformations (see Fig. 1): 7–8, 4–5, 5–6 and 6–7. As reported earlier, the heat of flue gases leaving the high temperature turbine of topping cycle is recovered in HRSG to produce water steam for the bottoming cycle (6–7). The produced stream is expanded in the high pressure turbine (HPT) to produce a certain shaft work in a conventional steam turbine (7–8). A part of the exhausted gas leaving HPT (point 8 of Fig. 1) is injected into CMB, the remainder is diverted into CCU as process steam to permit methane reforming. As reported in the previous section the stream leaving HRSG is divided into two parts. One of these, as reported before, is compressed in COMP. The remainder is subject to a low-pressure steam expansion (4–5) taking place in a conventional low pressure steam turbine (LPT). Such a turbine is equipped with a standard condenser (pressure value is set according to the amount of incondensable steam present in the stream). As mentioned before for (0–1), the dashed line (8–1) represents the irreversible mixing process involving the compressed steam water leaving COMP (1) and the output stream of HPT (8). The bottoming cycle is a sort of Rankine cycle where conventional steam turbine (i.e. HPT and LPT) produce useful work.

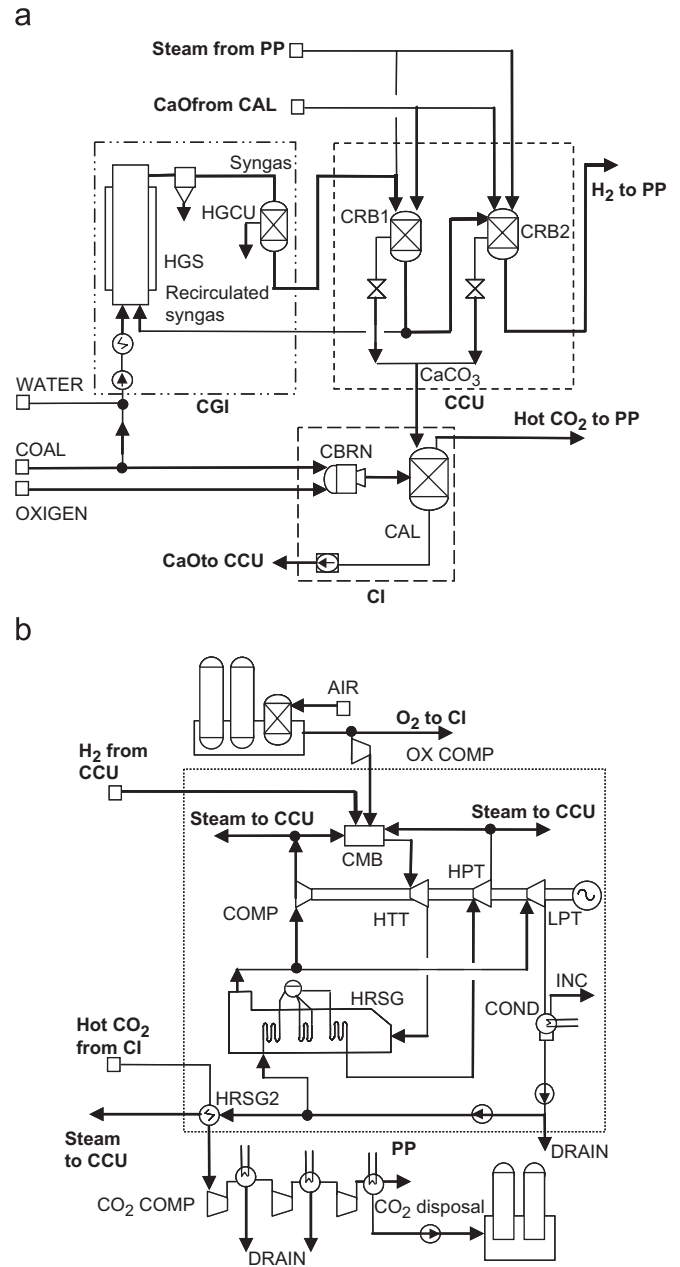


Fig. 2. (a) and (b) Plant 1 layout.

2.4.3. HRSG description

As depicted in Fig. 5, the HRSG can be broken into an economizer (ECO), an evaporator (EVA) and a superheater (SUR). The water leaves the condenser COND is pumped up to 200 bar to enter ECO and cool the flue gases down to 120°C . So the liquid water leaving the ECO is diverted into the EVA where the occurrence of boiling is considered. When the water is completely evaporated a minimum degree of superheat in EVA is considered. Finally, the water steam leaving EVA enters SUR to produce a superheated steam (200 bar, 600°C) for performing, into the bottoming cycle, the expansion in HPT. No pressure drops are hypothesized in HRSG.

3. Plant configuration description

Because the equilibrium pressure of CO₂ increases with increasing temperature according to the following function proposed [6]:

$$P_{Ae} = 4.137 \times 10^7 e^{-20474/T} \text{ bar}$$

and because the calcination will advance if the partial pressure of CO₂ is lower than its equilibrium pressure, the sorbent regeneration needs to be performed at the lowest possible pressure. To this end, two different plant configurations have been developed, called “plant 1” and “plant 2”, respectively. In the former an atmospheric calcination process is conducted; in the latter the sorbent regeneration is envisioned at a pressure level equal to the one of CCUs. In addition to CI, these two configurations differ for the power island.

3.1. Description of “plant 1”

“Plant 1” represents the base case configuration proposed by the ZECOMIX project sponsored by ENEA. Figs. 2(a) and (b) show the scheme of the “plant 1”.

The main components of this configuration are, grouped by section:

- **Gasification island:** The main parameters of this section are reported in Table 1. A slurry-based hydrogasifier would be preferable to avoid steam-pressurized lock-hoppers and related storage equipment. Slurry feeds the gasifier, where it reacts with the recycle flow (6) downstream the high temperature carbonator to form methane. Recycle flow contains 70% of the syngas outgoing from the high temperature carbonator of the CO₂ capture island. A minimum value of recycle fraction is required to guarantee a complete coal reaction.
- **CCU.** Steam feeds both carbonators to perform the reforming process. The higher the steam mass flow rate, the higher the conversion of methane into hydrogen. The temperature range required by the chemical kinetics of the reactions imposes a limit on the steam mass flow rate [2]. As reported in Table 2, all processes take place at 30 bar.

Uptake of CO₂ from the reaction zone will drive the equilibrium controlled reactions to completion. As a result a high conversion of CH₄, CO and H₂O in the low temperature decarbonization reactor takes place at a

Table 1
Terms for coal gasification island

Terms	Unit	Plant 1	Plant 2
Coal input to gasifier	kg/s	1	1
Slurry heating temperature	°C	150	150
Gasifier pressure	bar	30	30

Table 2
Terms for CO₂ capture unit

Terms	Unit	Plant 1	Plant 2
Carbonator pressure	bar	30	30
Temperature of CRB1 carbonator	°C	750	750
Temperature of CRB2 carbonator	°C	600	600
Process steam temperature	°C	350	350
Syngas recycle ratio	%	70	70

Table 3
Terms for calciner island

Terms	Unit	Plant 1	Plant 2
Calciner pressure	bar	1	30
Calciner temperature	°C	950	1200

temperature (600 °C) lower than conventional reforming temperature (800 °C).

- **CI.** The products of CI are an off-gas, composed mainly of CO₂, and a solid outlet of calcium oxide. The heat needed to regenerate the CO₂-acceptor is obtained by combustion of coal. In order to avoid high temperature ranges, a portion of the CO₂ produced in the calciner is mixed with O₂ and sent to the coal burner as combustion's moderator. As Table 3 displays, calciner process takes place at 950 °C and 1 bar. The hot CO₂, leaving CI is generated by the coal combustion process, and solid sorbent regeneration. This gaseous stream shall be sent to a recovery boiler (HRSG2), dried and diverted to compressors for CO₂ storage.

The heat recovered by the (HRSG2) is needed to produce a part of the steam required by the gasification island. The regenerated CaO is sent to CCU. Thus, this calciner option involves the hot solid handling between CCU and CI, increasing the potential for wear and erosion of pumps, valves and pipes. As a consequence, technical problems may exist in moving the solid sorbent CaO through the pressure gap existing between CCU and CI. Such a limitation, particularly the erosion of pumps and valves, will be overcome by conceiving a calciner whose operating pressure is the one of the CCUs. In such a calciner, to be introduced later in “plant 2”, there is no need for valves and pumps.

- **Power plant.** Syngas, leaving the gasification island, is composed mainly of water, hydrogen and oxygen; it enters the combustion chamber at 30 bar. An oxy-combustion is performed while a steam flow is sent into the combustion chamber (COMB) as a temperature moderator. The combustion gas, mainly composed of steam (mass fraction $w = 99.5\%$), is sent to a high temperature turbine (HTT). The exhaust steam downstream the HTT is characterized by a pressure of 1 bar. It enters the recovery boiler and produces high pressure and temperature steam (200 bar and 600 °C,

respectively). The water steam produced is sent to an HPT where it expands down to 30 bar. The exhaust steam, outgoing the recovery boiler, is split in two streams: one feeds the LPT, the other one feeds the steam compressor (COMP). The former stream expands up to a pressure value depending on incondensable gases in the working fluid. In order to achieve a zero emission carbon, these incondensable gases, composed mainly of CO₂, can be diverted to CI. The condensate downstream the condenser of LPT is sent to the recovery boiler. A portion of it is discharged and sent to an external recovery boiler (HRSG2), fed by the hot CO₂ stream outgoing from the calciner reactor. A part of the water steam downstream HPT is mixed with a portion of the steam leaving the steam compressor and sent as inlet to the gasification island. Table 4 shows a summary of the main terms of the power plant.

3.2. Description of “plant 2”

In addition to COMP and HTT, solid processing is a complex and crucial part of the “plant 1” within the CaO and CaCO₃ treatment facilities because of erosion and wear of valves, pipes and pumps used for hot solids handling.

The second plant configuration has been developed to avoid hot solid handling and steam compressor in “plant 1”. Let us use the syngas to fuel the calciner and produce a part of the water steam demanded by the chemical section. This implies some changes in both the plant scheme and the thermodynamic cycle of the power plant section. An overview of the selected plant configuration is depicted in Figs. 3(a) and (b). As shown earlier for “plant 1”, the layout of “plant 2” is made up of the following areas.

- Gasification island and CCU. The devices of the gasification island and CCU are the same of those reported in “plant 1”. The main difference is the splitter (SPT) that diverts the raw syngas leaving the hydro-gasifier through CI.

Table 4
Terms for power plant

Terms	Unit	Plant 1	Plant 2
Gas turbine inlet temperature	°C	1400	1400
Compressor outlet max temperature	°C	660	–
HPT inlet temperature	°C	600	–
HPT inlet pressure	bar	200	–
HRSG pressure (hot path)	bar	1	1
HRSG outlet Temperature (hot path)	°C	120	120
HRSG minimum temperature delta	°C	> 10	> 10
Turbine adiabatic efficiency	%	90	90
Compressor adiabatic efficiency	%	85	85
Pump efficiency	%	75	75
Electric generator efficiency	%	97	97

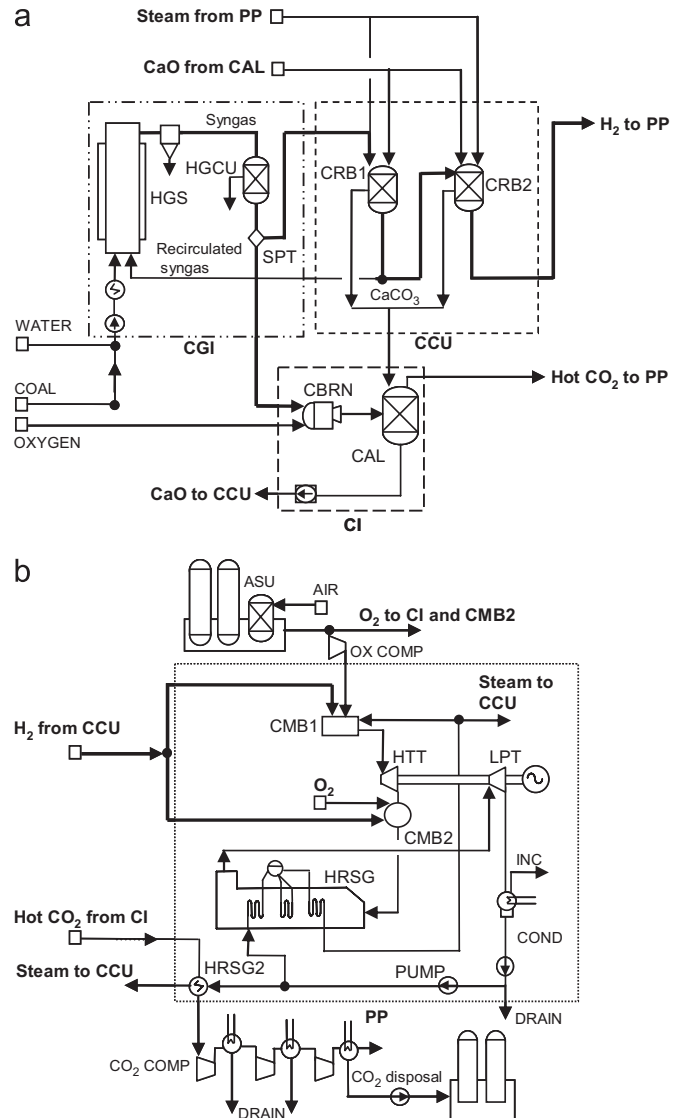


Fig. 3. (a) and (b) Plant 2 layout.

- CI. The calciner is fuelled by raw syngas leaving the gasification island. The calcination process is carried on at 30 bar and 1200 °C. The oxy-combustion of syngas takes place with steam supply in order to have a low CO₂ partial pressure and hence a good CaO regeneration efficiency. The regenerated CaO is then sent to CCU as a CO₂-acceptor. Technical problems do not occur in moving CaO, as CI and CCU work at the same pressure. Then the combustion gases are sent to the recovery boiler (HRSG2) in order to produce a part of the steam rate required from the chemical island.
- Power plant. The key point of this configuration is that the power island, reported in Fig. 1, cannot provide the heat needed to produce the steam required by the other sections. Since the basic power island is unable to satisfy the calciner and chemical steam demand, a different steam cycle is conceived (Fig. 4). In the main combustion chamber (CMB1) an oxy-combustion takes place at

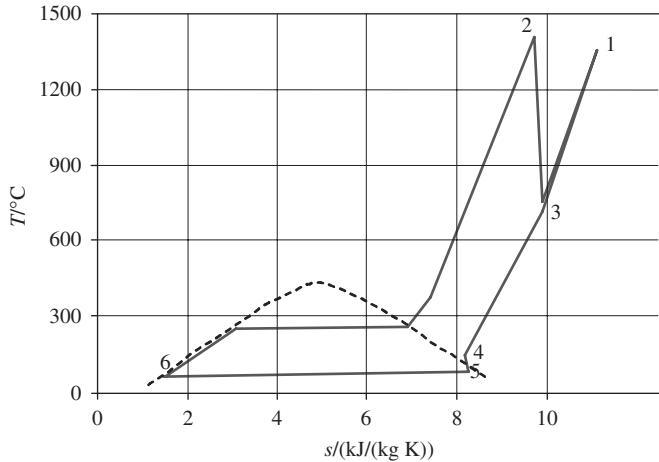


Fig. 4. Modified ZECOTECH cycle.

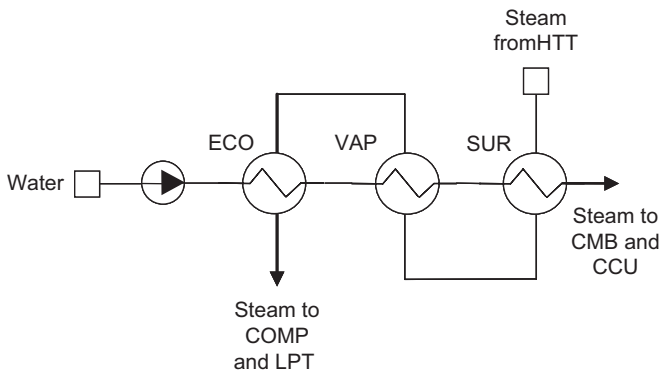


Fig. 5. HRSG scheme.

30 bar, and a water steam rate is injected in this device as the temperature moderator. A part of the syngas that supplies the CMB1 is split in an additional combustion chamber (CMB2) in which the oxy-combustion takes place. The temperature moderator in CMB2 is sent to the flue gases exiting the HTT. Then the flue gases leaving the CMB2 are driven to an atmospheric HRSG in order to produce a part of the water steam demanded by the chemical section and the steam required as the temperature moderator in CMB1. The exhaust gases leaving the HRSG are sent to the LPT and expand as in “plant 1” (Fig. 5).

4. Plant comparison

Information needed for scale-up to an industrial process using fluidized bed technology for pre-combustion and CO₂ capture is currently not available in the literature. Plant comparison is based on the following assumptions.

1. The hydrogasifier, carbonators and calciner are conceived as adiabatic fluidized beds. Thus, a continuously

stirred tank reactor appears as the most suitable to model these reactors, because it states temperature homogeneity throughout the reactor’s volume.

2. The considered coal is the Pittsburgh #8 one.
3. No heat and pressure losses occur in pipes, chemical reactors and heat exchanger.
4. Energy required for moving solid and compressing CO₂ has not been accounted for.
5. The stoichiometric amount of CaO has been considered in the carbonation-reforming process.
6. Coal Low Heating value enthalpy, $h_{LH} = 29,000$ kJ/kg.

Calculations were carried out by using the same set of assumptions as quoted in Tables 1–4. Configurations accounting for performances of both the gasification island and of the power section are compared. Because the gasification process has unavoidable losses due to the conversion of part of chemical energy into thermal we consider the LHV-based cold gas (CG) efficiency defined as follows:

$$\eta_{CG} = SCMR \frac{h_{LH,SYN}}{h_{LH,COAL}} \times 100\%, \quad (1)$$

where $h_{LH,SYN}$ is the low heating massic enthalpy of that syngas and SCMR represents the syngas to coal mass ratio defined as the mass flow rate of syngas transferred to the power island (w_{SYNPP}), referred to the mass flow rate of coal entering the gasification and CIs. Mathematically

$$SCMR = \frac{w_{SYNPP}}{w_{COAL,CGI} + w_{COAL,CI}}, \quad (2)$$

where $w_{COAL,CGI}$ and $w_{COAL,CI}$ are, respectively, the mass flow rate of coal enters CGI and CI. It worth noting that for “plant 2” configuration w_{CI} is zero.

The overall efficiency of the whole plant based on produced electrical energy (E_{ELE}) and the chemical energy of coal used to run the plant (E_{CHE}) is defined in a canonical way, as

$$\eta = \frac{E_{ELE}}{E_{CHE}} \times 100\%. \quad (3)$$

4.1. Electrical energy

The electrical power produced by the proposed energy system was calculated by means of the following expression:

$$W_{ELE} = \eta_{GEN} \cdot (|W_{EXP}| - W_{AUX}), \quad (4)$$

where W_{EXP} is the actual power of expanders, W_{AUX} represents the auxiliary power demand and η_{GEN} is the electric generator efficiency (assumed to be 0.97).

The actual power of expanders was estimated by the following expression:

$$-W_{EXP} = w_{HTT}\Delta h_{HTT} + w_{HPT}\Delta h_{HPT} + w_{LPT}\Delta h_{LPT}, \quad (5)$$

where w_{HTT} , w_{HPT} and w_{LPT} represent, respectively, the mass flow rate enters *HTT*, *HPT* and *LPT*; instead Δh_{HTT} ,

Δh_{HTT} and Δh_{LPT} are correspondingly the change in massic enthalpy of the above-mentioned streams.

In the same manner W_{AUX} was calculated by means of:

$$W_{AUX} = w_{COMP}\Delta h_{COMP} + w_{OX\ COMP}\Delta h_{OX} + w_{CO_2}\Delta h_{CO_2}(w_{OX\ COMP} + w_{OX\ CI}) \cdot h_{ASU}, \quad (6)$$

where w_{COMP} , $w_{OX\ COMP}$, $w_{OX\ CI}$ and w_{CO_2} are, respectively, the mass flow rate enters the COMP, OX COMP, CI and CO₂ compressors; instead Δh_{COMP} , Δh_{OX} and Δh_{CO_2} are correspondingly the change in massic enthalpy of the aforesaid streams. In addition, h_{ASU} represents the energy demand to produce oxygen in air separation unit (ASU) and $w_{OX\ CI}$ is the mass flow rate of oxygen used in calciner. The former parameter was estimated on the value recommended in [7] ($h_{ASU} = 826$ kJ/kg).

4.2. Chemical power

Finally, the chemical power derived from the coal which is used to fuel the CGI and CI was calculated by multiplying the mass flow rate of coal entering CGI ($w_{COAL\ CGI}$) and CI ($w_{COAL\ CI}$) and the low heating massic enthalpy of this fuel ($h_{LH\ COAL}$), that is to say:

$$W_{CHE} = h_{LH,COAL} \cdot (w_{COAL\ CGI} + w_{COAL\ CI}), \quad (7)$$

where, as reported earlier, W_{CHE} is the chemical power of coal entering the gasification and CI.

4.3. Hydrogen production

The objective of this process is to produce both electrical energy and hydrogen. Considering a scenario where the automotive sector is based on hydrogen, “plant 1” configuration can be easily adapted to be an “all hydrogen” production plant. Replacing the power island with a conventional boiler, the steam required by the process can be produced. The adopted solution supposes the boiler to be fed by a part of the syngas. The massic production of hydrogen from coal at standard conditions is 1.9 m³/kg. The composition of the high H₂-content syngas is shown in Table 4.

5. Results and discussions

As the thermodynamics analysis of ZECOMIX concept, reported in Section 2, has confirmed the feasibility of a TSSEMR process (CO₂ capture and methane reforming followed by regeneration sorbent) for the production of hydrogen, efforts are made to compare the different plant configuration using the efficiencies defined in Section 4.

Referring unit mass of coal feeding the whole plant, “plant 1” configuration produces syngas, mainly composed by hydrogen and water steam. Small amounts of methane and CO₂ still remain. “Plant 2” configuration produces almost the same amount of syngas per unit mass of coal (i.e. the parameter SCMR shows almost the same value in the two different plant configurations as reported in

Table 5). In addition, the electrical energy and the auxiliary energy demand for all devices were calculated as well as the energy required to yield the oxygen by means of ASU. Finally, for TSSEMR process, steam flow rate (needed in CCU) and fuel consumption (requested by CI) were obtain.

5.1. Comparison of performance

Comparison of performance is being conducted to select one promising plant configuration for the producing hydrogen and electricity with CO₂ capturing. The analyzed parameters include the overall efficiency, η , the CG efficiency, η_{CG} . In addition the vapor to coal mass ratio (VCMR) produced by the investigated configurations was performed. Such a parameter is defined as

$$VCMR = \frac{w_{VAPOR}}{w_{COAL\ CGI} + w_{COAL\ CI}}. \quad (8)$$

Based on our assumptions, “plant 1” uses an atmospheric calcination process for regenerating the CO₂-acceptor. This configuration is the base case of comparison. In Table 6 the chemical power (E_{CHE}), the actual work of expanders (W_{EXP}) and auxiliary power demand (W_{AUX}) of the two configurations are reported. As reported in table, the CG efficiency is larger for “plant 1” (62.7%) than “plant 2” (50.3%). Plant configurations differ for water steam produced in power plant (VCMR). This parameter was estimated to be, for “plant 1” and

Table 5
Syngas comparison

System parameter	Unit	Plant 1	Plant 2
SCMR	kg/kg	2.6	2.7
$h_{LH,SYN}$	kJ/kg	7291	5488
<i>Syngas composition</i>			
x_{H_2}	%	41.34	34.16
x_{N_2}	%	0.17	0.17
x_{H_2O}	%	57.40	63.74
x_{CH_4}	%	1.06	1.84
x_{CO}	%	0.01	0.02
x_{CO_2}	%	0.02	0.07

Table 6
Performances comparison of plants

System parameter	Unit	Plant 1	Plant 2
Chemical power E_{CHE}	MW	41.36	29.76
Actual power of expanders W_{EXP}	MW	33.91	9.55
Auxiliary power demand W_{AUX}	MW	14.90	3.01
Vapor to coal mass ratio $VCMR$	kg/kg	3.38	6.54
η_{CG}	%	62.7	50.3
η	%	45.9	21.9
		49.3 ^a	23.7 ^a

^aThe calculation is carried out omitting power demand to compress the CO₂ and pump it up to 80 bar.

“plant 2”, respectively, 3.38 and 6.54 kg/kg. This difference in VCMR is attributable to the different steam demand in calcinations process. In fact, the main characteristic of “plant 2” is to perform the calcination process at the same operating pressure as the CCU, avoiding the technological needs associated with the pressure gaps between these two sections. Since the calcination process in “plant 2” takes place at high pressure level, it is necessary to inject steam in order to reduce the partial pressure of CO₂. This allows the calciner to work at 30 bar but it implies a high steam request (Table 6). This difference in the steam demand implies also significant changes in the power island: this is at expense of “bottoming section” of ZECOTECH cycle. In fact, considering “plant 2”, such a cycle is unable to generate the required quantity of steam; it is necessary to “cut” the bottoming cycle to produce the needed steam. This modification in thermodynamic cycle implies a reduction of the overall efficiency. In fact, the overall efficiency for “plant 1” configuration is approximately 50%, whereas for “plant 2” an overall efficiency was estimated to be about 24%. Notice that, although

ZECOMIX plant produces an overall efficiency in the vicinity of 50% lower than the efficiency (60%) performed in some conventional gasification combined cycle, the TSSEMR process integrated in the investigated plants will reduce CO₂ emissions.

In conclusion, the simulation results show that using part of the produced raw syngas instead of coal for firing the calciner, the chemical power demand is decreased at the expense of a reduced CG and overall efficiency. The difference in the performance value suggests to invest in technology development of “plant 1” configuration (Tables 6 and 7).

5.2. Mole balance of carbon

Analysis of simulation results on the investigated process provides useful information to make an inventory of carbon over the two different analyzed configurations. The carbon content of the input and output streams of the main devices in the investigated configurations is presented in Tables 8 and 9. The carbon-based compounds to be analyzed are C, CH₄ and CO₂. It worth to note that the molar flowrate of carbon entering coal gasification island (named $n_{IN CGI}$) is balanced from the molar flowrate of calcium carbonate from CCU to CCI ($n_{CCU CI}$) and the methane molar flowrate leaving CCU to power plant ($n_{CCU PP}$):

$$n_{IN CGI} = n_{CCU CI} + n_{CCU PP}. \quad (9)$$

The last expression for the “plant 2” has the flowing form:

$$n_{IN CGI} = n_{CCU CI} + n_{CCU PP} + n_{IN CI} \quad (10)$$

to take in account a part of raw syngas leaving CGI and used as fuel in CI ($n_{IN CI}$).

Table 7
H₂-rich syngas composition

Parameter	Unit	Plant 1
SCMR	kg/kg	0.216
Syngas LHV	kJ/kg	101,000
<i>Syngas volume fraction</i>		
x_{H_2}	%	96.7
x_{N_2}	%	0.37
x_{H_2O}	%	0.17
x_{CH_4}	%	2.40
x_{CO}	%	0.10
x_{CO_2}	%	0.26

Table 8
Molar inventory of carbon in “Plant 1”

System parameter	Unit	$n_{IN CGI}$	$n_{CCU CI}$	$n_{IN CI}$	n_{DISP}	$n_{OUT CI}$	$n_{CCU PP}$	n_{COND}
n_C	mol/s	61.3	–	24.0	–	–	–	–
n_{CH_4}	mol/s	–	–	–	–	–	3.3	–
n_{CO_2}	mol/s	–	–	–	82.0	–	–	3.1
n_{CaCO_3}	mol/s	–	58.0	–	–	–	–	–
Total	mol/s	61.3	58.0	24.0	82.0	–	3.3 ^a	3.1 ^a

^aThese values do not satisfy formula (13) because a certain amount of CO₂ dissolves in drain leaving power plant (PP).

Table 9
Molar inventory of carbon in “Plant 2”

System parameter	Unit	$n_{IN CGI}$	$n_{CCU CI}$	$n_{IN CI}$	n_{DISP}	$n_{OUT CI}$	$n_{CCU PP}$	n_{COND}
n_C	mol/s	61.3	–	–	–	–	–	–
n_{CH_4}	mol/s	–	–	8.2	–	–	1.4	–
n_{CO}	mol/s	–	–	1.3	–	–	–	–
n_{CO_2}	mol/s	–	–	1.8	51.4	–	0.1	1.5
n_{CaCO_3}	mol/s	–	48.6	–	–	8.5	–	–
Total	mol/s	61.3	48.6	11.3	51.4	8.5	1.5	1.5

The term $n_{CCU PP}$ is due to the fact that syngas leaving CCU and diverted to PP contains a certain amount of carbon-based compounds (see Table 5).

The streams of solids mainly composed calcium carbonate and unreacted calcium oxide leaving carbonators are processed in CI. The energy requirement for solid sorbent regeneration is provided by heat released during the combustion of coal calciner (or syngas in “plant 2” configuration). The molar flowrate of carbon entering CI ($n_{IN CI}$) is burned and the yielded CO_2 is mixed with the CO_2 released during $CaCO_3$ calcination ($n_{CCU CI}$). As a consequence molar flow rate of CO_2 sent to HRSG2 in PP and then to CO_2 disposal (n_{DISP}) takes in account for CO_2 obtained from burning coal or syngas in calciner as well as the CO_2 released from regeneration solid sorbent. Mathematically:

$$n_{IN CI} + n_{CCU CI} = n_{DISP}. \quad (11)$$

The last expression written for the “plant 2” has the flowing form:

$$n_{IN CI} + n_{CCU CI} = n_{DISP} + n_{OUT CI}, \quad (12)$$

where $n_{OUT CI}$ represents the unreacted calcium carbonate leaving CI. If any carbon generation occurs in PP, carbon-based input stream ($n_{CCU PP}$) is equal to carbon-based output stream leaving COND (n_{COND}), that is to say

$$n_{CCU PP} = n_{COND}. \quad (13)$$

Next we compare, respectively, the left and right sides of Eqs. (9) and (11). This yields the following expression:

$$n_{IN CGI} + n_{IN CI} = n_{DISP} + n_{COND}. \quad (14)$$

In the same way comparing Eqs. (10) and (12), for “plant 2” configuration we obtain

$$n_{IN CGI} = n_{DISP} + n_{COND}.$$

The last two expressions simply say that the carbon flow rate entering the energetic system is balanced by carbon flow rate diverting to CO_2 disposal and leaving COND. Finally, if the incondensable gases leaving COND with a certain CO_2 flow rate (n_{COND}) are diverted in CI, the GHG atmospheric emission is zero.

6. Conclusions

Within the framework of the emerging clean coal technologies, a novel thermodynamic cycle, named ZECOMIX, has been investigated. In this paper we want to point out how the integration of different areas, composing this plant, can play a key role in enhancing the overall net efficiency. The first part of this paper was focused on thermodynamics of ZECOMIX concept in order to demonstrate the feasibility of a TSSEMR process. In such a process it is realized by combining the reforming and shift reactions with simultaneous removal of the CO_2 produced in the aforementioned reactions by means of solid sorbent, so that hydrogen yield is enhanced. The CO_2 will be in situ captured from the reaction zone by

calcium-based solid sorbent, resulting in a pure product stream of hydrogen. As solid material has become soaked with CO_2 , it will be driven to CI, where a process of sorbent thermal regeneration takes place. The power section is based on an innovative combined cycle, named ZECO-TECH that uses steam as working medium in both the “topping” and “bottoming” sections.

Particularly, the novelty introduced in the investigated energetic system is the production of hydrogen by means of an exothermic coal hydrogasification followed by a TSSEMR process. Hence no energy input is demanded in coal gasification island (CGI). The raw syngas from the gasification island is fed through a pressurized reforming and decarbonization step simultaneously at 30 bar. The highly enriched hydrogen syngas produced can be burned directly in the power plant, or be stored for industrial or automotive purposes. Because CI affects the performance of the process as a whole, the remainder of this paper was focused on comparison of two possible plant flowsheets: “plant 1”, which is the base case, and “plant 2” which differ from each other regard to CI. As a consequence, changes in power plant have to be introduced to account the different CI option.

In “plant 1” configuration the calciner is fuelled by coal and the calcination process is performed at atmospheric pressure by means of flue gas produced by the oxy-combustion of coal. Hence, the sorbent regeneration is conducted at a different pressure respect to CO_2 separation process (30 bar) and a circulation of solid between CCU and CI is stated. As noted before, such a configuration has some technical issues: any process involving circulation of solids between the areas operating with different pressure levels, increases the potential of erosion and wear of valves, pipes and pumps. A possible solution to solid circulation between CCU and CI in “plant 1” is feeding calcium carbonate and calcium oxide as slurry and using a screw pump to achieve the operating pressure of carbonators which was established to be 30 bar.

In order to overcome these problems, “plant 2” configuration was proposed. In such a configuration, a part of raw syngas leaving CGI is fed through CI. The heat needed to regenerate solid sorbent is obtained by flue gases releasing from the burning that raw syngas with an oxygen stream. As a result, the regeneration process is conducted at a pressure equal to the pressure of CCU and no pump for solid circulation is needed. A major drawback of this technical option is the higher steam demand of calciner. In fact, because of the higher operating pressure water steam is injected in calciner to reduce partial pressure of CO_2 . Moreover, the ZECO-TECH cycle was modified to account for an higher steam demand. In particular, a part of decarbonized syngas leaving CCU is burned into an additional combustor and the flue gases are diverted to HRSG to produce the requested steam stream. As a result the bottoming section of ZECOTECH cycle was cut to make steam production possible.

Comparison of overall efficiency was performed to select one good-looking plant configuration for the producing hydrogen and electricity with CO₂ capturing. The main result shows that “plant 1” with an atmospheric calciner is a promising technology option achieving a higher overall efficiency in the vicinity of 50%. Even if some commercially combined cycle produce somewhat higher efficiency close to 60% without a CO₂ capturing process, “plant 1” has the potential to efficiently produce energy and hydrogen with no CO₂ emissions, mitigating GHG releases in atmosphere. Finally, material science issues such as reducing erosion in solid circulation paths need to be addressed. As a consequence, there is a need to better understand the effect of the CO₂-acceptor on the erosion of pumps and valves in the hot solid handling paths. Additional research is requested to investigate the behavior of the steam compressor. The high efficiency of ZECOMIX reference plant makes an investment in developing this clean coal technology valuable. Alternative solutions, based on conventional gasification process and traditional CO₂ removal (i.e. amine and physical absorption), do not reach efficiencies higher than 36–42%. Moreover, the ZECOMIX system shows an efficiency comparable to other innovative options, like the Graz [8] and MATIANT [9] cycles.

Acknowledgment

The authors wish to thank the Italian ministry for research for the financial support of the project FISRT-TEPSI within the National Programme of Integrated Hydrogen and Power Production.

References

- [1] Sugisita H, Mori H, Uematsu K. A study of thermodynamic cycle and system configurations. *Int J Hydrogen Energy* 1998;23(8):705–12.
- [2] Ziok H, Lackner K. Overview of the ZECA (zero emission coal alliance) technology. Report number LA-UR-00-6002, DOE contract number W-7405-ENG-36. Research organization, Los Alamos National Laboratory; 2000.
- [3] Stendardo S, Girardi G, Calabrò A, Deiana P, Foscolo PU. A model for the uptake of a gaseous compound by a particulate sorbent: the case of carbon dioxide sequestration with dolomite. In: *Proceedings of the clean coal technologies 2007 (CCT2007)*, Italy, 2007.
- [4] Xiu G, Soares JL, Li P, Rodrigues AE. Simulation of five-step one bed sorption-enhanced reaction process. *Am Inst Chem Eng* 2002; 48(12):2817–32.
- [5] Lee DK, Baek IH, Yoon WL. Modelling and simulation for the methane steam reforming enhanced by in situ CO₂ removal utilizing the CaO carbonation for H₂ production. *Chem Eng Sci* 2004;59: 931–42.
- [6] Stanmore BR, Gilot P. Review—calcination and carbonation of limestone during thermal cycling for CO₂ sequestration. *Fuel Process Technol* 2005;82:1707–43.
- [7] Mathieu P. Presentation of an innovative zero-emission cycle for mitigating the global climate change. *Int J Appl Thermodyn* 1998;1.
- [8] Jericha H, Göttlich E, Sanz W, Heitmeir F. Design optimisation of the Graz cycle prototype plant. *J Eng Gas Turbines Power* 2004; 126:733–40.
- [9] Mathieu I. Towards the hydrogen era using near-zero CO₂ emissions energy systems. *Energy* 2004;29:1993–2002.
- [10] Abanades JC, Anthony EJ, Lu DY, Salvador C, Alvarez D. Capture of CO₂ from combustion gases in a fluidized bed of CaO. *Am Inst Chem Eng J* 2004;50(7).
- [11] Gambini M, Guizzi GL, Vellini M. H₂/O₂ cycles: thermodynamic potentialities and limits. *J Eng Gas Turbines Power* 2005;127: 553–63.
- [12] Gambini M, Vellini M. Advanced mixed cycles based on steam–methane reforming and air blown combustion. Paper presented at the international joint power generation conference, Atlanta, Georgia, USA, 2003.
- [13] Lin S, Harada M, Suzuki Y, Hatano H. Hydrogen production from coal by separating carbon dioxide during gasification. *Fuel* 2002;81: 2079–85.
- [14] Gallucci K, Stendardo S, Foscolo PU. CO₂ capture in hydrogen production from renewable sources. Paper presented at HYSY-Days—2nd world congress of young scientists on hydrogen energy systems, Turin, Italy; 2006.
- [15] Lin S, Harada M, Suzuki Y, Hatano H. Developing an innovative method, HyPr-RING, to produce hydrogen from hydrocarbons. *Energy Convers Manage* 2002;43:1283–90.
- [17] Calabrò A, Deiana P, Fiorni P, Stendardo S, Girardi G. The ZECOMIX experimental facility for hydrogen and power generation from coal. Paper presented at 8th international conference on greenhouse gas control technologies, Trondheim, Norway; 2006.
- [18] Calabrò A, Deiana P, Fiorni P, Stendardo S, Girardi G. A comparison between ZECOMIX high efficiency zero emission plant and hydrogen and power IGCC plants. Paper presented at H2www@Sicily, Second international conference on hydrogen era, 2005.
- [19] Jericha H, Sanz W, Woisetschläger J, Fesharaki M. CO₂-retention capability of CH₄/O₂-fired Graz cycle. Paper presented at CIMAC Conference, Interlaken, Switzerland; 1995.
- [20] Sugisita H, Mori H, Uematsu K. A study of thermodynamic cycle and system configurations of hydrogen combustion turbines. *Int J Hydrogen Energy* 1998;23(8):705–12.