INNOVATIVE ENERGY CONVERSION SYSTEMS BY CHEMICAL LOOPING: CONCEPTUAL DESIGN, MODELING AND SIMULATION, THERMAL INTEGRATION AND PERFORMANCE EVALUATION

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ABSTRACT

Development of efficient and environmental friendly technologies for fossil fuels conversion is of great importance in the modern society. Along this line, the Carbon Capture, Utilization and Storage (CCUS) technologies are important for transition to a low carbon economy. Chemical looping methods attracted much attention in the last decade as a promising energy conversion system able to deliver high energy efficiency coupled with inherent CO_2 capture. This paper evaluates the power generation as well as energy vectors poly-generation systems based on chemical looping systems with almost total decarbonisation (carbon capture rate higher than 95%) of the used fuel. As illustrative example, an iron-based chemical looping system was assessed in various configurations using both gaseous and solid fuels. To illustrate the poly-generation systems, hydrogen & power and Synthetic Natural Gas (SNG) & power co-generation cases were considered as examples. The evaluated chemical looping-based systems generate about 400 - 500 MW net power with a flexible hydrogen output in the range of 0 to 200 MW_{th} (lower heating value - LHV). The SNG and power co-generation case evaluated an 800 MW_{th} SNG thermal output (LHV) with a limited power output.

INTRODUCTION

The industrial sector is facing multiple challenges in the attempt to curb its greenhouse gas (GHG) emissions as well as securing the primary energy supply to satisfy the continuous growing energy consumptions, while improving the economic competitiveness. Economic and political frameworks are being putting in place to stimulate the development of energy-efficient low carbon industrial solutions [1]. For instance, the European Union (EU) is committed to reduce its greenhouse gas emissions by at least 40% compared to 1990 levels by 2030 and by 85 – 90% by 2050. Other relevant EU energy and environmental targets to be accomplished by 2030 are aiming to increase the renewable energy sources share in the energy mix at least 27% and reducing by at least 27% the energy consumption by increasing the energy efficiency.

The transition to a low-carbon economy can only be realized through the acceleration of development of a diverse portfolio of low-carbon energy conversion technologies [2], which, in turn, will enable the timely commercialization and large-scale deployment of these technologies in the energy sector as well as in other energy-intensive industrial applications (e.g. cement, metallurgy, chemicals etc.).

Chemical looping is an emerging carbon capture method suitable to be applied in advanced energy conversion processes [3]. This method is promising in delivering both high energy efficiency and low CO_2 emissions. The main advantages of chemical looping conversion are: inherently CO_2 capture with no significant ancillary energy duty (compared to gas-liquid absorption), high temperature heat recovery potential (which contribute to the increasing of overall energy efficiency), a variety of gaseous, liquid and solid fuels can be used etc.
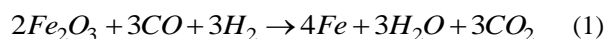
The paper evaluates the potential usage of chemical looping systems for power generation as well as for energy vectors poly-generation based on fossil fuels. As poly-generation capability, hydrogen / SNG and power co-generation scenarios were evaluated. The capacity to produce a flexible hydrogen (or other energy carrier like SNG, methanol, liquid fuels) output is an important aspect for integration in modern energy conversion systems where power plant cycling to meet the grid time demand variations is mandatory.

The evaluated concepts are generating about 400 - 500 MW net electricity with a flexible hydrogen output in the range of 0 to 200 MW_{th}. The carbon capture rate of evaluated concepts is almost total (>95%). A SNG and power co-generation case is also presented. The paper presents in details the plant configurations, operational aspects as well as mass and energy integration issues. The chemical looping conceptual designs were modelled and simulated using process flow modelling software (ChemCAD). The mass and energy balances are then used to assess the overall performance indicators (e.g. energy efficiency, ancillary consumption, carbon capture rate, specific CO_2 emissions etc.). For comparison reason, the benchmark concepts without carbon capture and with carbon capture using gas-liquid absorption were also considered. As the results show, the chemical looping systems have significant advantages compared to the benchmark cases, the more important being higher energy efficiency, lower plant ancillary consumptions and plant complexity and reduced CO_2 emissions.
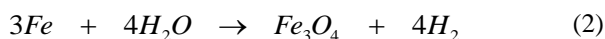
CHEMICAL LOOPING CONVERSION

In order to avoid the nitrogen contamination which complicates the CO_2 separation, the chemical looping systems implies the usage of a solid oxygen carrier (usually a metallic oxide of Fe, Ni, Mn, Cu etc.) to totally or partially oxidize the fuel [4,5]. Several independent reactors (most of them operated in circulating fluidised bed mode) are used: in the first reactor (called fuel reactor), the fuel is oxidised with the oxygen carrier to CO_2 and water; the second reactor (steam reactor) is used for oxygen carrier partial oxidation with steam to produce a stream of hydrogen (used for power generation or poly-generation purposes) and the third reactor (air reactor) is for the total reoxidation of the oxygen carrier with air. The chemical reactions involved in an iron-based looping system considering syngas as fuel as well as the operating temperatures of the three reactors are presented below:
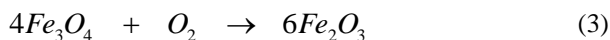
- Fuel reactor (operated as $700 - 750^{o}C$):

$$2Fe_2O_3 + 3CO + 3H_2 \rightarrow 4Fe + 3H_2O + 3CO_2 \quad (1)$$

- Steam reactor (operated as $700 - 800^{o}C$):

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad (2)$$

- Air reactor (operated as $850 - 1000^{o}C$):

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \quad (3)$$

The air reactor has a double operational purpose: to completely reoxidise the oxygen carrier to be recycled to the fuel reactor and to maintain the thermal balance of the whole system (the fuel conversion is an endothermic process since the oxygen carrier reoxidation processes are both exothermic). The solid oxygen carrier flow is also used to transport heat from steam / air reactors to the fuel reactor. The conceptual layout of iron-based chemical looping cycle for fossil fuel conversion is presented in Figure 1.
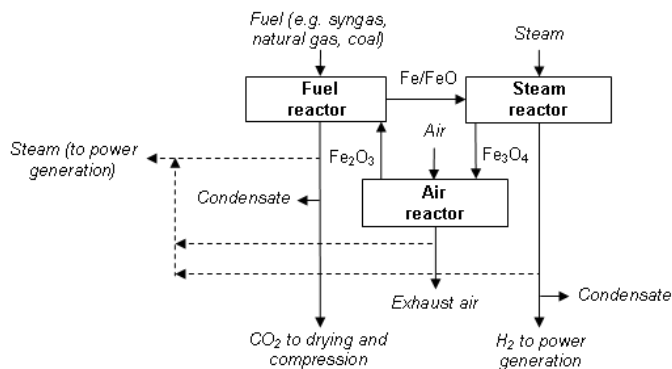
Figure 1 Conceptual layout of three reactor iron-based chemical looping system

The hydrogen stream produced in the steam reactor can be used for power generation in a hydrogen-fuelled combined cycle gas turbine or for poly-generation purposes (e.g. hydrogen and power co-generation as investigated in this paper). Other energy carriers like synthetic fuels (as showed for SNG case) can be also a promising option to evaluate [6,7].

PLANT CONFIGURATIONS & MODEL ASSUMPTIONS

As illustrative cases, one gaseous fuel (syngas produced by coal gasification) and one solid fuel (coal) were considered. The evaluated chemical looping cases were compared to benchmark cases (IGCC plants without carbon capture and with carbon capture using gas-liquid absorption - Selexol^{TM}).

The following cases were evaluated:
Case 1: Syngas-based chemical looping;
Case 2: Coal-based chemical looping;
Case 3: IGCC power plant without carbon capture;
Case 4: IGCC power plant with carbon capture (Selexol^{TM}).

Figure 2 presents the conceptual layout of syngas-based chemical looping system for energy vectors poly-generation (Case 1). Beside hydrogen and power generation mentioned already above, the Figure 2 considers also the synthetic hydrocarbons production e.g. Substitute Natural Gas (SNG) or Fischer-Tropsch (FT) fuel.
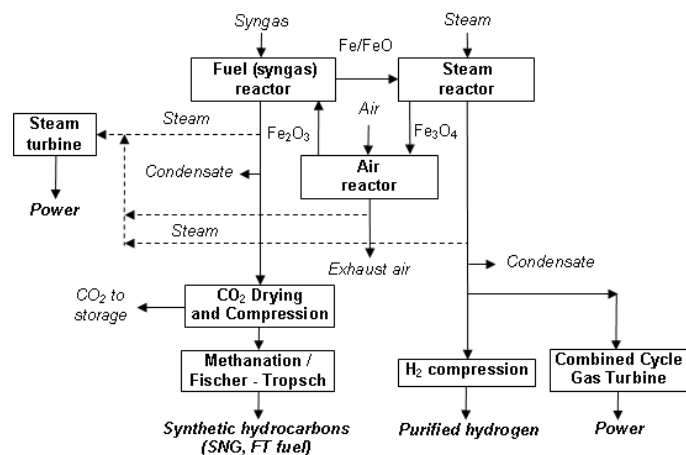
Figure 2 Conceptual layout of chemical looping system for energy vectors poly-generation

For the coal-based chemical looping system (Case 2) the layout is similar with the one presented in Figure 2 for the syngas case. Some differences still exist regarding the solid fuel transport and introduction system in the fuel reactor. The fuel reactor for the coal-direct case can be designed either in fluidised mode (as for the syngas case) or in a moving-bed mode [8,9]. In both cases, additional gases (e.g. steam or CO_2) have to be used for transport the fuel. Another significant difference for solid fuel looping cycles is that the oxygen carrier flow gets impurified with ash. A make-up of fresh oxygen carrier and an ash removal system has to be introduced.

As primary fuel considered in all cases, a high grade coal sort (Douglas Premium) was considered. For cases which incorporate a gasifier (Cases 1, 3 and 4), the coal-based Shell gasification process was considered. The main reasons for selecting Shell gasifier are the high cold gas efficiency and the fact that the generated syngas is clean of pyrolysis products. As the power block, a Combined Cycle Gas Turbine (CCGT) unit was considered using one M701G2 (Mitsubishi Hitachi Power Systems) gas turbine. The reasons for choosing this gas turbine are high energy efficiency (39.5% net) and the operational

experience on hydrogen-rich gases. In all cases, in the steam cycle of the CCGT unit were integrated the steam flows generated in the rest of the plant (e.g. gasification island, chemical looping cycle). Detailed thermal integration of the evaluated concepts was done using pinch method for overall energy optimisation [10].

Table 1 presents the main plant design assumptions for all evaluated cases (including the benchmark cases).

Table 1 Main plant design assumptions

| Unit	Parameters
Air separation unit (Cases 1, 3 & 4)	Oxygen purity: 95% (vol.) Power consumption: 200 kWh/ton O_2
Shell gasifier (Cases 1, 3 & 4)	Entrained-flow gasifier Gibbs free energy minimization model Pressure: 40 bar; Temperature: >1400ºC Pressure drop: 1.5 bar; Gas quench configuration
Acid gas removal (Cases 1, 3 & 4)	Solvent: Selexol^{TM} for H_2S capture Solvent regeneration: Thermal
Iron looping cycle (Cases 1 & 2)	Oxygen carrier: ilmenite ($FeTiO_3$) Fuel reactor parameters: 30 bar / 700 - 750ºC Steam reactor parameters: 28 bar / 700 - 800ºC Air reactor parameters: 26 bar / 850 - 1000ºC Gibbs free energy minimization model Pressure drop: 1 bar / reactor
Gas-liquid absorption (Case 4)	Solvent: Selexol^{TM} for CO_2 and H_2S capture Solvent regeneration: Thermal and pressure flash
CO_2 compression and drying unit	Delivery CO_2 pressure: 120 bar Solvent for CO_2 drying: Tri-ethylene-glycol Captured CO_2 specification (vol. %): >95% CO_2; <2000 ppm CO; <250 ppm H_2O; <100 ppm H_2S
H_2 compression unit	Delivery pressure: 60 bar Hydrogen purity: 99.95% (vol.) Compressor efficiency: 85%
Gas turbine	Gas turbine: M701G2 (MHPS) Net output: 334 MW; Net efficiency: 39.5%
Heat recovery steam generation (HRSG)	Pressure levels: 120 bar / 34 bar / 3 bar One medium pressure (MP) steam reheat Steam turbine isoentropic efficiency: 85% Steam wetness ex. steam turbine: max. 10%
Heat exchangers	$\Delta T_{min.} = 10$ºC; Pressure drop: 3 - 5% of inlet pressure

MODELING, SIMULATION & PROCESS INTEGRATION

All energy conversion concepts were modelled and simulated using process flow modelling software (ChemCAD). As thermodynamic model used in the simulations, thermodynamic equilibrium has being assumed for calculations (e.g. gasification, chemical looping cycle, gas-liquid absorption etc.). The choice of thermodynamic equilibrium was considered taking into account the high operating temperatures for the thermo-chemical conversion units [11]. Soave-Redlich-Kwong (SRK) equation of state with Boston-Mathias modifications was used as thermodynamic package. Since all carbon capture designs were equipped with a CO_2 drying unit, TEG Dehydration thermodynamic package was considered. Regarding the gasification island and the chemical looping cycle, Gibbs free energy minimization reactor was used. The developed mathematical models and the simulation results were validated against experimental data [8,9,12].

All plant concepts were modelled and stimulated in a fully thermally integrated design, which means that all the heating duties needed for various processes are based on available hot

streams within the plant. The only energy input is the coal feedstock. The coal input was calculated through simulation in order to produce the hydrogen stream to fire one M701G2 gas turbine (334 MW net power output).

Pinch analysis was used as main heat and power integration analysis tool. For better energy integration, the plants were split in two sub-systems, one being thermo-chemical conversion of coal (via chemical looping and / or gasification) and other being the power block. 10ºC was considered as minimum temperature differences in the analysis. As illustrative example, the hot and cold composite curves (HCC and CCC) are presented in Figures 3 (gasification island and chemical looping cycle) and 4 (CCGT-based power block) for the syngas-based chemical looping concept (Case 1).
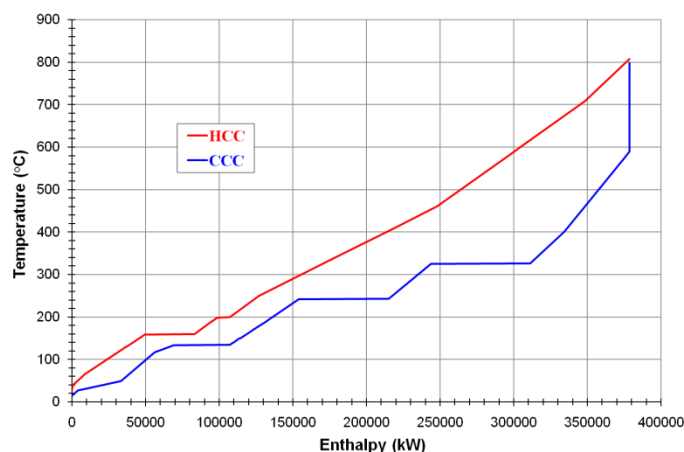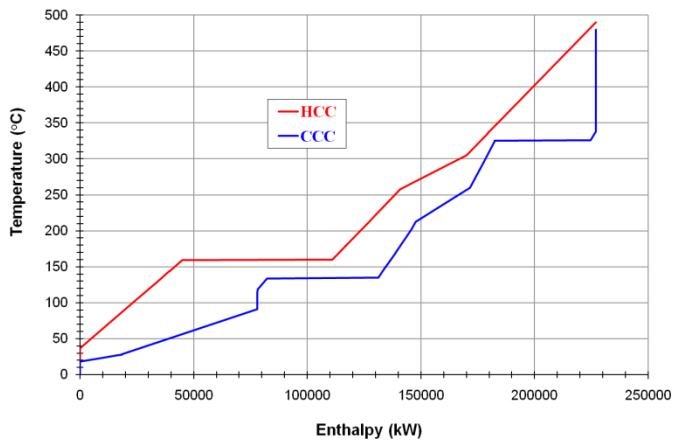

Figure 3 Hot and cold composite curves for gasification island and chemical looping cycle (Case 1)
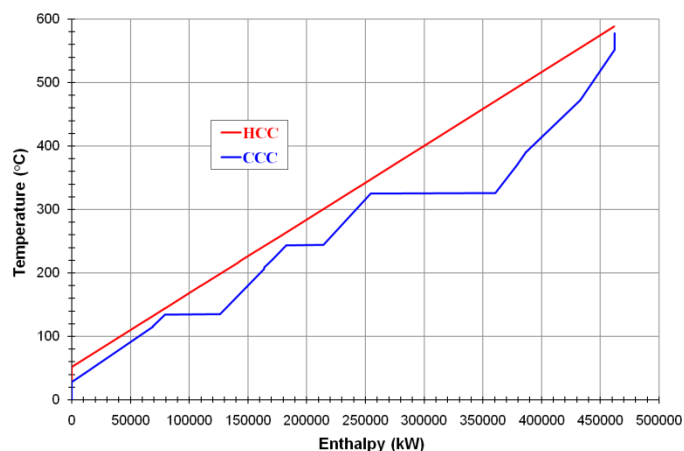
Figure 4 Hot and cold composite curves for hydrogen-fuelled combined cycle gas turbine (Case 1)

As can be observed from Figures 3 and 4, the thermal integration was done very tight in order to increase the overall energy efficiency. As it was mention above, one particular advantage of chemical looping systems represents the high temperature heat recovery potential compared to CO_2 capture

based on gas-liquid absorption. The operational parameters of the chemical looping reactors make available heat sources at high temperatures. This heat can be used for high pressure steam generation with benefic consequences on the overall energy efficiency of the plant. In contrast, in pre-combustion capture based on gas-liquid absorption, the carbon capture unit is operated at near ambient temperatures due to solvent constraints which means that the heat in available al low temperature. For comparison reason, Figure 5 presents the hot and cold composite curves for gasification island and absorption-based carbon capture unit (Case 4).

Figure 5 Hot and cold composite curves for gasification island and absorption-based CO_2 capture unit (Case 4)

As can be noticed from Figure 5, the heat recovery potential, in both available heat and supply temperatures, is significantly lower for the gas-liquid absorption case than for the chemical looping case. Other mass and energy integration options were assessed [13]. For instance, the air integration analysis between the Air Separation Unit (ASU) and the gas turbine compressor was evaluated as a method to further improve the plant efficiency. Figure 6 presents the variation of net power efficiency vs. air integration degree for Case 1.
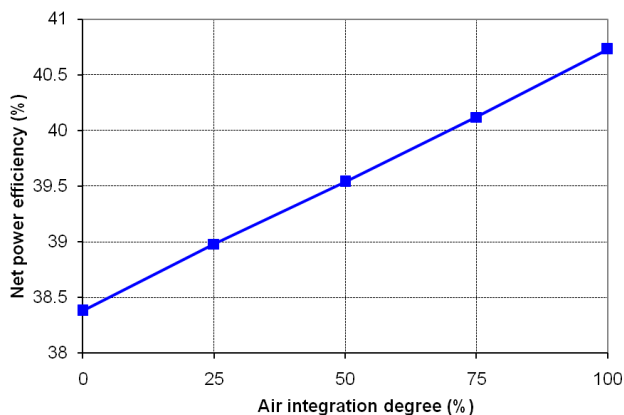
Figure 6 Air integration analysis between air separation unit and gas turbine (Case 1)

After simulation, process and thermal integration analysis, the overall mass and energy balances are produced for all evaluated cases. These data were then used for assessing the key plant performances (e.g. gross and net power output, energy efficiency, ancillary consumptions, carbon capture rate, specific CO_2 emissions etc.).

RESULTS AND DISSCUSSIONS

The first evaluated operational mode of investigated concepts is the power generation only. In this operational mode the whole hydrogen stream is used to fire the gas turbine. This operation is more feasible in short to medium term until large scale energy vectors poly-generation systems (e.g. hydrogen and power co-generation, synthetic fuels etc.) are become widely available. Table 2 presents the key performance indicators for the evaluated cases.

Table 2 Key plant performance indicators
(power generation only)

Main Plant Data	Units	Case 1	Case 2	Case 3	Case 4
Coal flowrate	t/h	162.34	149.90	147.80	165.70
Coal calorific value	MJ/kg	25.353			
Coal thermal energy	MW_{th}	1143.28	1055.67	1040.88	1166.98
Gas turbine output	MW_e	334.00	334.00	334.00	334.00
Steam turbine output	MW_e	199.45	153.78	224.01	210.84
Expander output	MW_e	1.50	60.63	0.68	0.78
Gross power output	MW_e	534.95	548.41	558.69	545.62
Power consumption	MW_e	96.06	104.86	73.50	112.44
Net power output	MW_e	438.89	443.55	485.19	433.18
Gross efficiency	%	46.79	51.94	53.67	46.75
Net efficiency	%	38.38	42.01	46.61	37.11
CO_2 capture rate	%	99.55	99.81	0.00	90.79
CO_2 emissions	kg/MWh	3.08	3.99	741.50	86.92

As can be noticed from Table 2, all investigated cases generate about 433 – 485 MW net power. The net power efficiencies of carbon capture cases are around 37 – 42%. The energy penalty of CO_2 capture is between 4.6 and 9.5 net electricity percentage points. From energy efficiency point of view direct-coal chemical looping concept (Case 2) has the highest value among the carbon capture designs. From carbon capture rate, both chemical looping systems (Cases 1 and 2) have superior values compared to gas-liquid absorption system (Case 4). The results of power only operational mode show that the chemical looping systems have promising higher energy efficiency compared to more technologically mature gas-liquid absorption. The plant complexity is also in favour of chemical looping cases (especially the direct coal conversion).

As mentioned in Table 1, the quality specification of captured CO_2 stream is important for any CCS design [14]. The investigated carbon capture options (chemical looping and gas-liquid absorption) evaluated in this paper comply with the proposed specification of captured CO_2. However, attention must be paid for chemical looping systems when nitrogen is used as fuel transport gas to the gasifier / fuel reactor since this nitrogen end up in the captured CO_2 stream.

The second investigated plant operation scenario is based on flexible hydrogen / synthetic fuels and power co-generation.

The plant flexibility (cycling) is very important in the actual context of modern energy system in which the share of time irregular renewable energy sources (e.g. wind, solar) is increasing at high speed [15]. A flexible plant means that the plant core (gasification island, carbon capture unit etc.) will be operated full load most of the time and only the power block will be operated accordingly to the instant grid demand. When the power demand is low, other energy carriers (e.g. hydrogen, synthetic fuels) can be produced and eventually store to cover the peak situations. Another advantage of poly-generation systems laid in the fact that other energy carriers than electricity can be easily stored in large quantities.

The flexible operation of the power plant has important benefits in term of plant life and economics (e.g. taking advantage of power spot prices during the peak power demand) [16]. The analysis presented in this paper evaluates a flexible hydrogen output in the range of 0 to 200 MW_{th} (based on hydrogen lower heating value). In this operation range, the gas turbine can be gradually turned down to make available a hydrogen gas stream for external customers. Table 3 presents the variation of key plant performance indicators with the hydrogen output for direct coal chemical looping conversion (Case 2).

Table 3 Key plant performance indicators
(hydrogen and power co-generation)

Main Plant Data	Units	Power	Hydrogen and power co-generation	
Coal flowrate	t/h	149.90		
Coal calorific value	MJ/kg	25.353		
Coal thermal energy	MW_{th}	1055.67		
Gas turbine output	MW_e	334.00	290.35	252.55
Steam turbine output	MW_e	153.78	132.24	114.76
Expander power output	MW_e	60.63	59.93	59.70
Gross power output	MW_e	548.41	482.52	427.01
Hydrogen output	MW_{th}	0.00	100.00	200.00
Power consumption	MW_e	104.86	102.91	100.32
Net power output	MW_e	443.55	379.61	326.69
Gross efficiency	%	51.94	45.70	40.44
Net efficiency	%	42.01	35.96	30.94
Hydrogen efficiency	%	0.00	9.47	18.94
Cumulative efficiency	%	42.01	45.43	49.88
Carbon capture rate	%	99.81	99.81	99.81
CO_2 emissions (energy)	kg/MWh	3.99	3.69	3.36

One can noticed from Table 3 that the overall plant energy efficiency is increasing with the hydrogen output. This aspect illustrates the positive influence of plant flexibility (hydrogen co-production rate) on overall plant energy efficiency. It can be noticed also that ancillary power demand is decreasing with the hydrogen output which is also a positive fact.

Similar conclusions can be drawn for other energy vectors co-generation cases. Table 4 presents the situation of SNG production based on direct coal chemical looping conversion (Case 2). In this analysis the focus was on SNG production (a thermal output of 800 MW was considered), the power generation being used to cover the plant ancillary consumption (no gas turbine was used, only steam turbine to use the excess steam generated in the plant).

Table 4 Key plant performance indicators
(SNG and power co-generation)

Main plant data	Units	Case 2
Coal flowrate	kg/h	167.45
Coal calorific value	MJ/kg	25.353
Coal thermal energy	MW_{th}	1179.32
Steam turbine output	MW_e	158.32
SNG thermal output	MW_{th}	800.00
Ancillary power consumption	MW_e	105.84
Net power output	MW_e	52.48
Net power efficiency	%	4.45
SNG thermal efficiency	%	67.83
Cumulative energy efficiency	%	72.28
Carbon capture rate	%	61.75
CO_2 emissions (SNG + power)	kg/MWh	7.37

As can be observed from Table 4, the cumulative plant energy efficiency is about 72% with a carbon capture rate slightly higher than 60% and very low CO_2 emissions. It must be realised that some of the coal carbon is present in SNG stream (a partial decarbonised energy carrier) and it will be released into the atmosphere when the SNG will be finally used. The carbon capture rate and specific CO_2 emissions were calculated considering the total carbon from the coal input. For a fully flexible SNG and power co-generation, some modifications need to be done to the power block (which will be based on a combined cycle similar to an NGCC plant).

An important conclusion that can be drawn from the evaluated co-generation cases is that there is always a trade-off between the fuel decarbonisation rate and the plant energy efficiency. As can be noted from the co-generation case of hydrogen and power (both totally decarbonised energy carriers), the cumulative energy efficiency is significantly lower than for the SNG and power co-generation (SNG is only a partial decarbonised energy carrier). In turn, the decarbonisation rate is almost total (>99%) for hydrogen and power co-generation while for SNG and power co-generation is much lower (~60%). This trade-off between fuel decarbonisation rate and plant energy efficiency has important consequences also on plant economics.

Other important aspects that emphasised the significant potential of poly-generation systems as innovative energy conversion methods for the future are [17-19]: combination of chemical synthesis routes (to produce chemicals with potential use as energy carriers) with power generation provided a promising option to increase the overall energy efficiency; one-pass poly-generation concepts produce synthetic fuels at lower cost than the recycle plants which target maximisation of the fuel production; poly-generation systems can provide decarbonised power at higher efficiency and lower environmental costs (CO_2 avoided) than the power plants designed only for power generation. In addition, a positive aspect of syngas-based chemical looping option represents the possibility to co-processing (co-gasification) fossil fuels with renewable fuels like various sorts of biomass, municipal solid wastes etc. Gasification process coupled with chemical looping for energy vectors poly-generation seems to be an innovative energy conversion technology for the future [20].

CONCLUSIONS

This paper evaluates via conceptual design, thermodynamic modelling and simulation and process integration tools, the key technical performances of chemical looping systems for energy vectors poly-generation. Iron-looping system was used to illustrate the main features of chemical looping method. Several illustrative looping cases using both solid and gaseous fossil fuels were presented and discussed in details to emphasize the main advantages of chemical looping technique as an innovative energy conversion technology to deliver high energy efficiency and low carbon emissions. Various mass and energy integration analysis were presented to illustrate the potential of further increase of energy efficiency.

Poly-generation concepts based on chemical looping were also discussed via illustrative examples of hydrogen & power and SNG & power co-generation cases. As described extensively within the paper, the poly-generation systems are very promising in delivering high energy efficiency coupled with almost total decarbonisation but also producing valuable chemicals / energy carriers. Benchmark coal-based gasification cases without carbon capture and with carbon capture using more technical and commercially mature gas-liquid absorption (Selexol^{TM}) were also considered.

The main conclusions supported by the presented results pointed out that the chemical looping is a very promising energy conversion method to deliver higher energy efficiency than conventional technologies (e.g. gasification, combustion, catalytic reforming) with almost total fuel decarbonisation (carbon capture rate higher than 99%). The energy vectors poly-generation applied to chemical looping systems give further increase of the overall energy efficiency.

ACKNOWLEDGEMENTS

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