CHEMICAL & CALCIUM LOOPING SYSTEMS: HEAT INTEGRATION ANALYSIS FOR IMPROVEMENT THE ENERGY EFFICIENCY OF VARIOUS INDUSTRIAL PROCESSES

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ABSTRACT

Improvement of energy efficiency for key industrial sectors is of great importance today considering the potential economic and environmental benefits. The carbon capture, utilization and storage (CCUS) technologies are considered strategically important technological options for transition to a low carbon economy. In this respect the chemical & calcium looping systems are very promising methods to deliver both high energy efficiency and near zero CO_2 emissions. This paper assesses the potential gains in term of energy efficiency for key illustrative fossil fuel-based industrial processes (e.g. combustion and gasification-based power plants, cement production plant, integrated steel mill, energy vector poly-generation systems etc.) by integration of chemical and calcium looping systems as carbon capture technologies. Two high temperature solid looping systems were evaluated in details: a chemical looping cycle using iron oxide as oxygen carrier and a calcium looping cycle using calcium-based sorbent. The carbon capture rate of all evaluated chemical & calcium looping concepts is almost total (>95%). As the detailed results show, the chemical & calcium looping systems exhibit superior energy efficiency, lower plant complexity and reduced CO_2 emissions in comparison to the more commercially and technologically mature carbon capture options (e.g. based on chemical or physical gas-liquid absorption).

INTRODUCTION

The heat and power sector as well as other energy-intensive industrial applications are facing significant challenges in the attempt to curb theirs fossil CO_2 emissions for transition to a low carbon economy [1]. The reduce the carbon footprint of energy-intensive processes as well as to increase the overall energy efficiency, the innovative solution need to be developed and deployed in industrial practice. To boost the development of energy-intensive processes with low fossil carbon emissions, technical, economic and politic instruments are used [2].

On the technological development front, the CCUS technologies are considered strategically important options for transition to a low carbon economy in the fight to reduce the greenhouse gas emissions and to combat the climate change [3]. Chemical & calcium looping methods are innovative high energy efficiency carbon capture method suitable to be applied in various energy-intensive industrial applications [4]. The high temperature looping methods are promising in delivering both high energy efficiency and low CO_2 emissions. The main advantages of chemical & calcium looping conversion are [5]: inherently CO_2 capture with no significant ancillary energy duty, high temperature heat recovery which contributes to the increasing of overall energy efficiency, fuel flexibility etc.

This paper assessed the potential advantages of chemical & calcium looping cycles in term of improving the energy efficiency for energy-intensive industrial processes (illustrative cases from various industrial sectors were selected). The chemical & calcium looping designs were thermodynamically modelled and simulated using process flow modelling software (ChemCAD). The improvement of the energy efficiency by heat integration analysis was carefully evaluated for various industrial size conceptual designs (e.g. about 500 MW net electricity power plants, 1 Mt/y cement production plant, 4 Mt/y integrated steel mill etc.). As the heat and power integration tool, the pinch method was used [6]. The mass and energy balances for the illustrative thermally integrated industrial size examples were then used to evaluate the overall performance indicators (e.g. energy efficiency, fossil fuel consumption, ancillary heat and power consumption, carbon capture rate, specific CO_2 emissions etc.). Benchmark cases of the investigated processes are also considered for comparison reasons in both situations: without carbon capture and with carbon capture using gas-liquid absorption.

CHEMICAL & CALCIUM LOOPING SYSTEMS

High temperature solid looping systems are promising option to reduce both energy and cost penalties for CO_2 capture. Two looping cycles were assessed in this paper in conjunction with various energy-intensive industrial applications. The first chemical looping system is based on iron oxides used as oxygen carrier for fuel oxidation. In the chemical looping systems, various oxygen carriers (usually metallic oxides of Ni, Fe, Cu, Mn etc.) are used to totally or partially oxidise the fuel [4]. The cycle involves two (for chemical looping combustion) or three (for combined heat & hydrogen production) interconnected fluidised bed reactors.

The chemical reactions in an iron-based chemical looping system considering syngas as fuel are presented below [7]:

- Fuel reactor (operated at 700 – 750^{o}C):

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

- Steam reactor (operated at 700 – 800^{o}C):

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

- Air reactor (operated at 850 – 1000^{o}C):

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

The iron-based chemical looping system can be used for process decarbonisation only in pre-combustion configuration (the process involving a gaseous, liquid or solid fuel). The conceptual layout of iron-based chemical looping cycle for hydrogen production is presented in Figure 1.

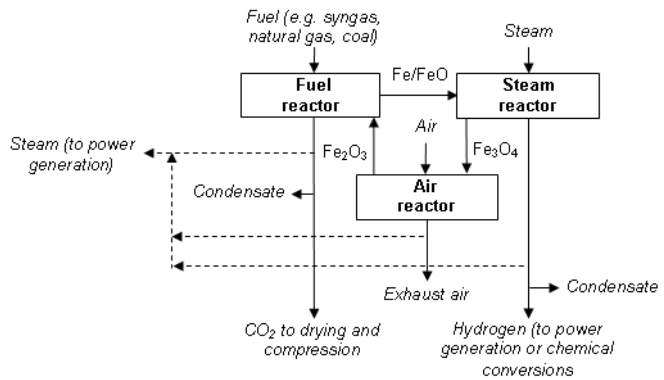

Figure 1 Conceptual layout of iron-based chemical looping system for hydrogen production coupled with carbon capture

The hydrogen produced in the steam reactor can be used either for power generation in a hydrogen-fuelled combined cycle gas turbine (CCGT) or for various chemical conversions (e.g. energy vectors poly-generation purposes).

The second looping system was based on calcium sorbent. This system involves two interconnected fluidised bed reactors where the following reactions take place [4]:

- Carbonation reactor (operated at 500 – 650^{o}C):

$$CaO + CO_2 \rightarrow CaCO_3 \quad (4)$$

- Calcination reactor (operated at 800 – 1000^{o}C):

$$CaCO_3 \rightarrow CaO + CO_2 \quad (5)$$

The calcium looping system can be used in both pre-combustion and post-combustion capture configurations. For pre-combustion capture, the calcium-based is used to shift to the right the equilibrium of water gas shift reaction (sorbent enhanced water gas shift - SEWGS):

$$CaO + CO + H_2O \rightarrow CaCO_3 + H_2 \quad (6)$$

The conceptual layout of calcium looping cycle (pre-combustion capture configuration - SEWGS) for combined hydrogen and power production is presented in Figure 2.

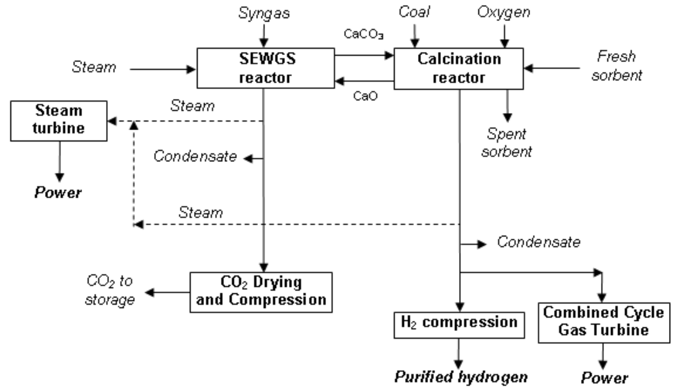

Figure 2 Conceptual layout of calcium looping system for hydrogen & power co-production coupled with carbon capture

PLANT CONCEPTS & MODEL ASSUMPTIONS

The following energy-intensive industrial processes were evaluated in conjunction with iron-based and calcium-based looping systems:

Case 1: Integrated gasification combined cycle (IGCC) plant;
Case 2: Super-critical pulverised coal (PC) power plant;
Case 3: Integrated steel mill;
Case 4: Cement production plant.

As primary fuel used in the evaluated cases, a high grade coal sort was considered. For assessed gasification concepts, Shell reactor was considered [8]. As the power block for IGCC concept, a Combined Cycle Gas Turbine (CCGT) unit was considered using one M701G2 (Mitsubishi Hitachi Power Systems) gas turbine. For super-critical PC power plant, the steam cycle has the following characteristics: 290 bar / 582^{o}C with two steam reheats (75 bar / 580^{o}C & 20 bar / 580^{o}C. In all cases, in the steam cycle of the power block was integrated the steam flows generated in the rest of the plant (e.g. gasification island, chemical looping cycle etc.). Detailed thermal integration of the concepts was done using pinch method for overall energy optimisation [9]. Table 1 presents the main plant design assumptions for evaluated cases.

Table 1 Main plant design assumptions

Unit	Parameters
IGCC power plant	Shell gasifier: operating at 40 bar & 1400^{o}C Acid gas removal: Selexol^{TM} One M701G2 gas turbine: net power output: 334 MW; net energy efficiency: 39.5% Heat recovery steam generation (HRSG): 120 bar / 34 bar / 3 bar with one MP reheat
Pulverised coal (PC) power plant	Main steam: 290 bar / 582^{o}C with two steam reheats Selective catalytic reduction unit (NO_x removal) Wet flue gas desulphurization unit (SO_x removal)
Integrated steel mill [10]	Capacity: 4 million t/y CO_2 capture from off gases, lime kilns, coke ovens
Cement plant [11]	Capacity: 1 million t/y Selective catalytic reduction unit (NO_x removal) Wet flue gas desulphurization unit (SO_x removal) Heat & power block: 130 bar / 535^{o}C
Iron looping cycle	Oxygen carrier: ilmenite ($FeTiO_3$) Fuel reactor parameters: 30 bar / 700 - 750^{o}C Steam reactor parameters: 28 bar / 700 - 800^{o}C Air reactor parameters: 26 bar / 850 - 1000^{o}C

Calcium looping cycle	Sorbent: natural limestone Carbonation reactor parameters: 500 - 650°C Calcination reactor parameters: 800 - 950°C Oxygen supply: 99% (vol.) purity & 220 kWh/t O_2
CO_2 compression and drying unit	Delivery CO_2 pressure: 120 bar Solvent for CO_2 drying: Tri-ethylene-glycol (TEG) 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.)
Heat exchangers	$\Delta T_{min.}$ = 10°C; Pressure drop: 3 - 5% of inlet pressure

MODELING, SIMULATION & PROCESS INTEGRATION

The evaluated concepts were modelled and simulated using process flow modelling software (ChemCAD). The simulations used several thermodynamic packages as follow: PPAQ for the combustion, gasification, gas treatment and steam generation processes; SRK for the calcium looping unit; Electrolyte for the MDEA-based gas-liquid absorption and TEG Dehydration for the captured CO_2 drying process using tri-ethylene-glycol (TEG). The developed mathematical models and the simulation results were validated against experimental data [10-13].

All concepts were modelled and stimulated in a fully thermally integrated design. Pinch analysis was used as main heat and power integration analysis tool with 10°C as minimum temperature difference. As illustrative examples, the hot and cold composite curves (HCC and CCC) are presented in Figures 3 (gasification island and looping cycle) and 4 (CCGT power block) for the IGCC power plant with pre-combustion carbon capture based on iron chemical looping (Case 1).

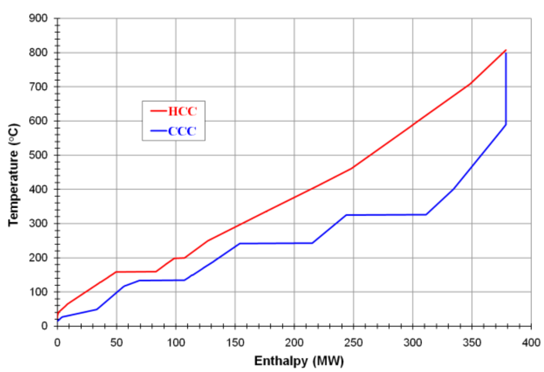

Figure 3 Hot and cold composite curves for the gasification island and chemical looping cycle (Case 1)

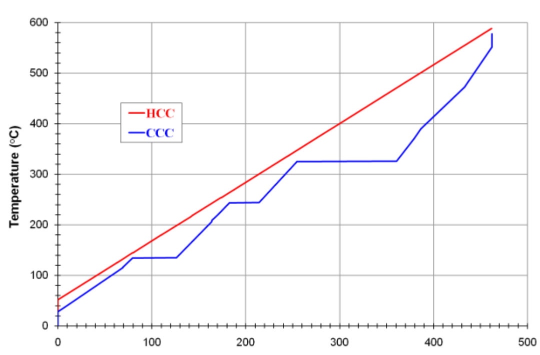

Figure 4 Hot and cold composite curves for the hydrogen-fuelled combined cycle gas turbine (Case 1)

Figure 5 presents the hot and cold composite curves (HCC and CCC) for the calcium-based looping unit used in conjunction with a pulverised coal (PC) power plant (Case 2).

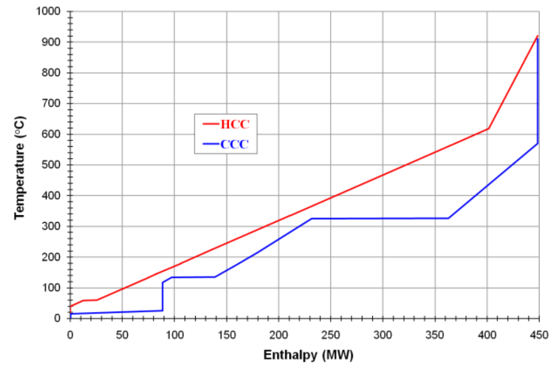

Figure 5 Hot and cold composite curves for the calcium looping cycle (Case 2)

As can be observed from Figures 3 to 5, 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 & calcium looping systems represents the high temperature heat recovery potential compared to other CO_2 capture methods e.g. gas-liquid absorption which operates at temperature near ambient (30 - 60°C).

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

RESULTS AND DISSCUSSIONS

The first evaluated energy-intensive application is based on coal gasification process. The same gasifier (Shell) was considered in all cases considering the performances of this reactor. Table 2 presents the key performance indicators for IGCC power plants (Case 1a: IGCC with pre-combustion CO_2 capture by iron looping; Case 1b: IGCC with SEWGS; Case 1c: IGCC without carbon capture and Case 1d: IGCC with pre-combustion CO_2 capture physical gas-liquid absorption by Selexol™).

Table 2 IGCC key plant performance indicators

Main Plant Data	Units	Case 1a	Case 1b	Case 1c	Case 1d
Coal flowrate	t/h	162.34	226.71	147.80	165.70
Coal calorific value	MJ/kg	25.353			
Coal thermal energy	MW_{th}	1143.28	1596.60	1040.88	1166.98
Gas turbine output	MW_e	334.00	334.00	334.00	334.00
Steam turbine output	MW_e	199.45	410.49	224.01	210.84
Expander output	MW_e	1.50	1.40	0.68	0.78
Gross power output	MW_e	534.95	745.89	558.69	545.62
Power consumption	MW_e	96.06	154.74	73.50	112.44
Net power output	MW_e	438.89	591.15	485.19	433.18
Net power efficiency	%	38.38	37.02	46.61	37.11
CO_2 capture rate	%	99.55	95.94	0.00	90.79
CO_2 emissions	kg/MWh	3.08	32.89	741.50	86.92

As can be noticed from Table 2, the pre-combustion CO_2 capture using iron looping cycle (Case 1a) has the highest energy efficiency compared to other carbon capture cases (the energy penalty for carbon capture is about 8.2 net electricity percentage points). In addition, the carbon capture rate of Case 1a is almost total (>99%) in comparison to other options. The calcium-based sorbent enhanced water gas shift concept (Case 1b) has energy efficiency comparable with the gas-liquid absorption concept (Case 1d) but the carbon capture rate is significantly higher (about 96%).

One promising option for gasification plants to further increase the energy efficiency is based on poly-generation scenario [14]. The flexible operation (cycling) of the power plant has important benefits in term of plant life and economics [15]. As an illustrative example, Table 3 presents the variation of key plant performance indicators with the hydrogen output (in the range of 0 to 200 MW_{th}) for Case 1a.

Table 3 Performances for hydrogen and power co-generation

Main Plant Data	Units	Power	Hydrogen and power co-generation	
Coal flowrate	t/h	162.34		
Coal calorific value	MJ/kg	25.353		
Coal thermal energy	MW_{th}	1143.28		
Gross power output	MW_e	534.95	478.75	421.75
Hydrogen output	MW_{th}	0.00	100.00	200.00
Power consumption	MW_e	96.06	97.10	98.25
Net power output	MW_e	438.89	381.65	323.50
Net power efficiency	%	38.38	33.38	28.29
Hydrogen efficiency	%	0.00	8.74	17.49
Cumulative efficiency	%	38.38	42.12	45.78
Carbon capture rate	%	99.55	99.55	99.55
CO_2 emissions (energy)	kg/MWh	3.08	2.81	2.58

As can be noticed from Table 3, the overall cumulative plant energy efficiency is increasing with the hydrogen output. This aspect illustrates the positive influence of plant flexibility on overall plant energy efficiency. In addition, energy vector poly-generation scenario brings better operational flexibility (ability to produce other energy carriers / chemicals) [16].

The second evaluated energy-intensive application was based on pulverised coal (PC) power plants. The pulverised fuel technology is the most widely used solid fuel power generation option [17]. Table 4 presents the key performance indicators for PC power plants (Case 2a: PC with post-combustion CO_2 capture by calcium looping; Case 2b: PC without carbon capture; Case 2c: PC with post-combustion CO_2 capture by gas-liquid absorption - MDEA).

Table 4 PC key plant performance indicators

Main Plant Data	Units	Case 2a	Case 2b	Case 2c
Coal flowrate	t/h	215.32	155.66	196.96
Coal calorific value	MJ/kg	25.353		
Coal thermal energy	MW_{th}	1516.42	1096.25	1387.12
Gross power output	MW_e	650.12	502.75	540.82
Power consumption	MW_e	107.24	28.01	65.15
Net power output	MW_e	542.88	474.74	475.67
Net power efficiency	%	35.80	43.30	34.29
CO_2 capture rate	%	92.75	0.00	90.00
CO_2 emissions	kg/MWh	68.95	800.10	92.52

As can be noticed from Table 4, the post-combustion capture using calcium looping (Case 2a) has the highest energy efficiency compared to the gas-liquid absorption case. The energy penalty for carbon capture in case of calcium looping is about 7.5 net electricity percentage points (lower than for the gas-liquid absorption case which is about 9 efficiency points).

The third energy-intensive application considered in this paper is integrated iron & steel mill. Many carbon capture scenarios can be envisaged for decarbonisation of an integrated steel mill [18] considering that this industrial sector is responsible for about 10-15% of total industrial primary energy consumption. This present analysis considered the decarbonisation of the steel mill off gases (CO_2 rich flue gases from the blast furnace, basic oxygen furnace, coke ovens, lime kilns and the captive power block).

Table 5 presents the key performance indicators for evaluated concepts: Case 3a: Steel mill with post-combustion CO_2 capture by calcium looping; Case 3b: Steel mill without carbon capture and Case 3c: Steel mill with post-combustion CO_2 capture by gas-liquid absorption - MDEA.

Table 5 Steel mill key plant performance indicators

Main Plant Data	Units	Case 3a	Case 3b	Case 3c
Fuel thermal energy	MW_{th}	1156.79	669.78	544.00
Gross power output	MW_e	457.10	224.68	309.64
Power consumption	MW_e	132.57	9.68	1.64
Net power output	MW_e	324.53	215.00	308.00
Net power efficiency	%	27.79	32.10	56.61
CO_2 capture rate	%	90.00	0.00	90.00
CO_2 emissions	kg/t HRC	640.01	2092.45	833.54

As can be noticed, the calcium looping systems ensures lower specific CO_2 emissions per tonne of hot rolled coil (HRC) than the gas-liquid absorption case (640 vs. 833 kg CO_2/t HRC). In addition, the spent calcium sorbent can be easily integrated into the steel plant (lime kilns are present in the conventional steel mill).

The last evaluated energy-intensive industrial application is the cement production. The cement production sector is responsible for about 5% of global CO_2 emissions [19]. Within the cement production process, CO_2 is produced both from fuel combustion as well as limestone decomposition.

Table 6 presents the main technical and environmental performance indicators for the evaluated concepts: Case 4a: Cement plant with post-combustion CO_2 capture by calcium looping; Case 4b: Cement plant without carbon capture and Case 4c: Cement plant with post-combustion CO_2 capture by gas-liquid absorption - MDEA.

Table 6 Cement production key plant performance indicators

Main Plant Data	Units	Case 4a	Case 4b	Case 4c
Fuel thermal energy	MW_{th}	153.81	-	234.06
Gross power output	MW_e	58.01	-	54.42
Power consumption	MW_e	42.19	16.24	34.14
Net power output	MW_e	15.82	-	20.28
Net power efficiency	%	10.28	-	8.66
CO_2 capture rate	%	90.00	0.00	90.00
CO_2 emissions	kg/t cement	58.37	770.44	55.83

As the results show, the calcium looping method has lower energy intensity (lower fossil fuel consumption by about 34%) that the gas-liquid absorption option for the same carbon capture rate (90% in both cases). In addition (as for the previous cases - the integrated steel mill), the spent calcium sorbent can be easily integrated into the cement production plant with more benefits in term energy consumptions.

In conclusion, the chemical and calcium looping methods have important advantages (higher energy efficiencies and carbon capture rate, potential integration of spent sorbent / oxygen carrier in the overall process) in comparison to the more technological and commercial mature CO_2 capture based on gas-liquid absorption [20].

CONCLUSIONS

This work assesses via conceptual design, thermodynamic modelling and simulation and thermal integration tools, the potential improvement in term of energy efficiency for the chemical and calcium looping technologies to be integrated into energy-intensive industrial applications. As illustrative examples, various fossil fuel-based industrial applications were selected: gasification and combustion-based power plants, iron & steel mill, cement production. As the results show, the iron-based chemical looping and the calcium looping options are promising methods to significantly reduce the energy penalty for the carbon capture in comparison to the gas-liquid absorption method.

In addition, the energy vector poly-generation concepts based on chemical & calcium looping cycles were also discussed via an illustrative example of hydrogen & power co-generation from the gasification plant with carbon capture by iron looping method. The flexible hydrogen and power co-generation scenario is promising in delivering high energy efficiency coupled with almost total fossil fuel decarbonisation. The further advantages of poly-generation systems lay in the potential use of produced hydrogen for further energy applications as well as for various chemical applications (e.g. production of synthetic fuels - methanol, Fischer-Tropsch etc.).

The main conclusions supported by the presented results pointed out that the chemical & calcium looping options are very promising energy conversion method to deliver higher energy efficiency than conventional technologies with high fuel decarbonisation rate (close to total carbon capture rate).

ACKNOWLEDGEMENTS

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REFERENCES

[1] International Energy Agency (IEA), Energy Technology Perspectives 2016: Towards Sustainable Urban Energy Systems, Paris, France, 2016

[2] European Commission, A policy framework for climate and energy in the period from 2020 to 2030, COM(2014) 15 final, Brussels, Belgium, 2014

[3] Metz B., Davidson O., de Coninck H., Loos M., and Meyer L., Carbon Dioxide Capture and Storage, *Intergovernmental Panel on Climate Change (IPCC)*, Geneva, Switzerland, 2005

[4] Fan L.S., Chemical looping systems for fossil energy conversions, Wiley-AIChE, 2010

[5] Adanez J., Abad A., Garcia-Labiano F., Gayan P., and de Diego L., Progress in chemical looping combustion and reforming technologies, *Progress in Energy Combustion*, Vol. 38, 2012, pp. 215-282

[6] Cormos C.C., Evaluation of energy integration aspects for IGCC-based hydrogen and electricity co-production with carbon capture and storage, *International Journal of Hydrogen Energy*, Vol. 35, 2010, pp. 7485-7497

[7] Tong A., Bayham S., Kathe M., Zeng L., Luo S., and Fan L.S., Iron-based syngas chemical looping process and coal-direct chemical looping process development at Ohio State University, *Applied Energy*, Vol. 113, 2014, pp. 1836-1845

[8] Cormos C.C., Economic implications of pre- and post-combustion calcium looping configurations applied to gasification power plants. *International Journal of Hydrogen Energy*, Vol. 39, 2014, pp. 10507-10516

[9] Smith R., Chemical processes: Design and integration, West Sussex, England, Wiley, 2005

[10] International Energy Agency - Greenhouse Gas R&D Programme (IEAGHG), Iron and steel CCS study (Techno-economics integrated steel mill), Report 2013/04, 2013

[11] International Energy Agency - Greenhouse Gas R&D Programme (IEAGHG), CO_2 capture in the cement industry, Report 2008/3, 2008

[12] International Energy Agency (IEA) - Greenhouse Gas R&D Programme (IEAGHG), Potential for improvement in gasification combined cycle power generation with CO_2 capture, Report PH4/19, 2003.

[13] NETL, Department of Energy, Cost and performance baseline for fossil energy plants, Vol. 1: Bituminous coal and natural gas to electricity. DOE/NETL-2007/1281, 2007

[14] Cormos C.C., Assessment of flexible energy vectors poly-generation based on coal and biomass/solid wastes co-gasification with carbon capture, *International Journal of Hydrogen Energy*, Vol. 38, 2013, pp. 7855-7866

[15] Brouwer A.S., van den Broek M., Seebregts A., and Faaij A., Operational flexibility and economics of power plants in future low-carbon power systems, *Applied Energy*, Vol. 156, 2015, pp. 107-128

[16] Meerman J.C., Ramírez A., Turkenburg W.C., and Faaij A.P.C., Performance of simulated flexible integrated gasification polygeneration facilities. Part A: A technical-energetic assessment, *Renewable and Sustainable Energy Reviews*, Vol. 15, 2011, pp. 2563-2587

[17] Davison J., Performance and costs of power plants with capture and storage of CO_2, *Energy*, Vol. 32, 2007, pp. 1163-1176

[18] Quader M.A., Ahmed S., Dawal S.Z., and Nukman Y., Present needs, recent progress and future trends of energy-efficient Ultra-Low Carbon Dioxide (CO_2) Steelmaking (ULCOS) program, *Renewable and Sustainable Energy Review*, Vol. 55, 2016, pp. 537-549

[19] Vatopoulos K., and Tzimas E., Assessment of CO_2 capture technologies in cement manufacturing process, *Journal of Cleaner Production*, Vol. 32, 2012, pp. 251-261.

[20] Cormos C.C., and Cormos A.M., Assessment of calcium-based chemical looping options for gasification power plants, *International Journal of Hydrogen Energy*, Vol. 38, 2013, pp. 2306-2317