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Reducing Carbon Footprint of Energy-Intensive Applications by CO_2 Capture Technologies: An Integrated Technical and Environmental Assessment

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Reducing the CO_2 emissions from energy production sector as well as from other energy-intensive industrial applications (e.g. metallurgy, cement, chemistry etc.) is of great importance today. Carbon capture, utilization and storage (CCUS) technologies are under development to be implemented in fossil fuel-based industrial applications to reduce the carbon footprint. The main aim of this paper is to present, through illustrative coal-based examples, the CO_2 capture technologies used to reduce the carbon footprint of energy-intensive processes. The assessments are focused on conceptual design, modelling and simulation, process integration and technical and environmental assessment of CO_2 capture with potential applications in industrial sectors with high greenhouse gas emissions e.g. power generation, metallurgy, cement, chemicals.
Two reactive gas-liquid and gas-solid carbon capture technologies are evaluated through illustrative industrial size examples. The CO_2 capture rate is set to 90 %. Various coal-based processes were considered as illustrative examples e.g. combustion, gasification, cement production, integrated steel mill, coal to chemicals etc. The proposed conceptual designs were modelled and simulated using process flow modelling software ChemCAD. The mass and energy balances as well as the thermal integration tools were used to quantify the key technical and environmental performance indicators (e.g. fuel consumption, overall energy efficiency, carbon capture rate, energy penalty for CO_2 capture, specific CO_2 emissions etc.). The integrated assessments show that CCUS technologies have significant advantages in reducing the environmental impact of energy-intensive industrial applications e.g. cutting the specific CO_2 emissions by about 60 - 90 %.

1. Introduction

Currently, the energy-intensive industrial sectors face significant challenges in term of reducing greenhouse gas emissions in an attempt to reduce global warming and climate change. Various technical measures can be applied to reduce CO_2 emissions e.g. improving energy efficiency, boosting renewable energy and large scale deployment of CO_2 capture, utilization and storage technologies. In respect to CO_2 capture options from industrial processes many technologies can be used e.g. gas-liquid absorption, oxy-combustion, gas-solid systems in pre-, post- and oxy-combustion configurations. Captured CO_2 can be either used as raw material to produce various chemicals / energy carriers (e.g. methanol, substitute natural gas etc.) or to be geologically stored in saline aquifers, depleted oil and gas fields or used for enhanced oil recovery (Metz et al., 2005).
This paper is evaluating the technical and environmental impact of CO_2 capture for several illustrative coal-based industrial processes e.g. power generation (both combustion and gasification systems), iron and steel, cement and chemicals. The first evaluated CO_2 capture option is based on a commercially mature (at least for chemical industry) gas-liquid absorption technology using reactive solvents (e.g. alkanolamines). The second CO_2 capture option is based on an innovative reactive gas-solid technology using calcium-based solid sorbents (calcium looping cycle). This new technology promises lower energy and cost penalties for CO_2 capture as well as higher energy efficiency compared to other more mature carbon capture options.

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The illustrative energy-intensive industrial applications (with and without CO_2 capture) were evaluated using modelling, simulation and process integration (Pinch analysis) tools, the mass and energy balances being then used to quantify key performance indicators. Main novelty elements of this paper are relating to propose an integrated assessment methodology of CO_2 capture in energy-intensive industrial applications, to provide up-dated values for performance indicators and to assess the potential mass and energy integration aspects.

2. Assessment methodology, main model assumptions and process integration

The first assessed reactive CO_2 capture method is based on gas-liquid absorption using alkanolamines (Methyl-DiEthanol-Amine - MDEA was considered as illustrative case in the present study). The CO_2 capture is based on absorption - desorption cycle according to the following reversible chemical reaction:

$$MDEA + CO_2 + H_2O \leftrightarrow MDEAH^+ + HCO_3^- \quad (1)$$

The second assessed reactive CO_2 capture method is based on a reactive gas-solid system using calcium-based sorbent (calcium looping). The CO_2 capture is based on carbonation - calcination cycle according to the following reversible chemical reaction:

$$CaO + CO_2 \leftrightarrow CaCO_3 \quad (2)$$

The conceptual designs of the two investigated CO_2 capture technologies (either in pre- or post-combustion capture configurations) based on reactive gas-liquid and gas-solid processes are presented in Figures 1 - 2.

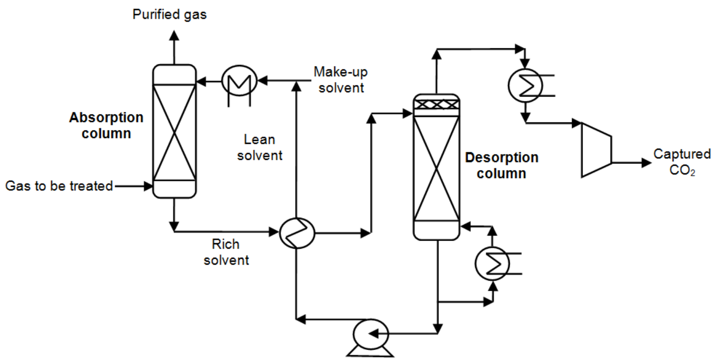

Figure 1: Conceptual design of CO_2 capture unit based on reactive gas-liquid absorption

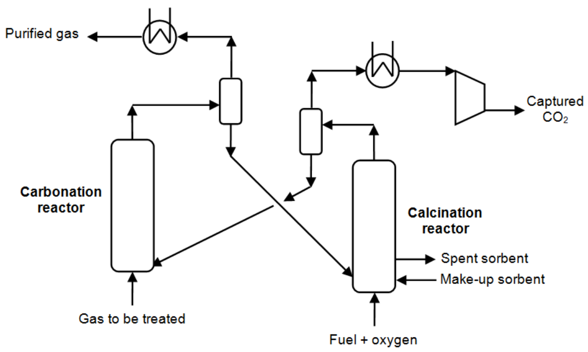

Figure 2: Conceptual design of CO_2 capture unit based on reactive gas-solid system (calcium looping)

The main energy penalty of gas-liquid absorption cycle is the thermal duty for solvent regeneration in the reboiler of the desorption column. For post-combustion capture systems, this energy penalty is about 3 MJ/kg CO_2. For calcium looping cycle, the need to provide heat to the calcination reactor ($CaCO_3$ decomposition is endothermic) implies the usage of additional fuel which is oxy-combusted but because the looping cycle is running at higher temperatures (500 - 900 °C which enhances heat recovery potential) than the absorption - desorption cycle (around ambient temperatures), the overall energy penalty is sensible lower than for gas-liquid absorption (6 - 7 vs. about 9 - 10 net efficiency percentage points for combustion-based power plants). The better heat recovery potential of calcium looping can be clearly noticed for Figure 3 which presents the Composite Curves for this system used in conjunction with a pulverised coal power plant (Klemeš, 2013).

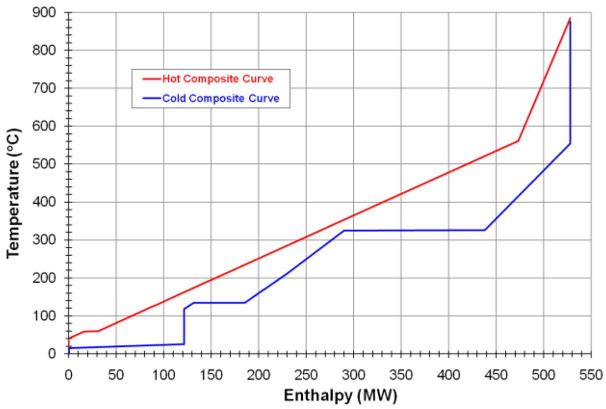

Figure 3: Composite Curves for a super-critical power plant integrated with calcium looping for CO_2 capture

Table 1 presents most important design assumptions used in assessment of investigated coal-based energy-intensive industrial applications (combustion and gasification power plants, integrated steel mill, cement plant) in which the two above mentioned reactive CO_2 capture methods were integrated. The similar cases without carbon capture were also considered as benchmark cases to quantify the CO_2 capture energy penalty.

Table 1: Design assumptions

Plant sub-system	Specifications
Coal characteristics	Composition (% wt. dry): 72.30 % carbon, 4.11 % hydrogen, 1.69 % nitrogen, 7.45 % oxygen, 0.56 % sulphur, 13.89 % ash; Moisture: 8 %; Lower calorific value (as received conditions): 25.17 MJ/kg
Pulverised coal power plant	Super-critical steam cycle: (290 bar / 582 °C) with two steam reheat (75 bar / 580 °C and 20 bar / 580 °C) with 500 MW net power output Selective catalytic reduction with 95 % NO_x removal efficiency Wet limestone desulphurisation with 98-99 % SO_x removal efficiency
Integrated gasification combined cycle (IGCC) power plant	Shell entrained-flow gasifier operated at 40 bar Acid gas removal based on MDEA for H_2S and CO_2 capture Combined cycle based on 1 x M701G2 gas turbine (334 MW net)
Cement plant	Capacity: 1 Mt/y cement Selective catalytic reduction with 95 % NO_x removal efficiency Wet limestone desulphurisation with 98-99 % SO_x removal efficiency
Integrated steel mill	Capacity: 4 Mt/y hot rolled coil (HRC) CO_2 capture from steam plant, hot stoves, lime kilns and coke ovens Heat and power block: Subcritical steam boiler (169 bar / 565 °C) with steam reheat (40 bar / 565 °C) / Combined cycle (HP 100 bar / MP 25 bar / LP 9 bar with MP reheat)
CO_2 capture unit based on reactive gas-liquid absorption cycle	Solvent: 50% aqueous solution of methyl-diethanol-amine (MDEA) Absorption column: 40 - 50 °C / Desorption column: 110 - 125 °C CO_2 capture rate: 90 %
CO_2 capture unit based on reactive calcium looping cycle	Sorbent: calcium-based sorbent (limestone) Carbonation reactor: 550 - 600 °C / Calcination reactor: 800 - 950 °C CO_2 capture rate: 90 %
Air separation unit (for calcination reactor of calcium looping cycle)	Oxygen purity (% vol.): 95 % O_2, 2 % N_2, 3 % Ar ASU power consumption: 200 kWh/t O_2
CO_2 compression & drying	Delivery pressure: 120 bar Compressor efficiency: 85 % Solvent used for CO_2 drying: TEG (Tri-ethylene-glycol) Captured CO_2 specification (vol. %): >95 % CO_2, <2,000 ppm CO, <250 ppm H_2O, <100 ppm H_2S, <4 % non-condensable gases
Heat recovery & steam turbine characteristics	Steam turbine isentropic efficiency: 85 % Steam wetness ex. steam turbine: max. 10 % Minimum approach temperature: $\Delta T_{min.}$ = 10 °C

3. Results and discussions

Various power plant technologies (combustion and gasification) and other energy-intensive industrial applications were simulated using ChemCAD in both non-capture and CO_2 capture scenarios. The mass & energy balances where then used for calculation of main technical and environmental indicators.

3.1 Super-critical pulverized coal power plants

The following super-critical coal-based power plants with 500 MW net output were evaluated: Case 1.1 - Super-critical power plant without carbon capture; Case 1.2 - Super-critical power plant with post-combustion CO_2 capture using a MDEA-based gas-liquid absorption system; Case 1.3 - Super-critical power plant with post-combustion CO_2 capture using a calcium looping system.
A conventional state-of-the-art super-critical pulverised coal power plant without carbon capture was considered as benchmark case (NETL, 2010). Table 2 presents the main technical and environmental performances for super-critical pulverized coal power plants with / without carbon capture. Both carbon capture cases have been evaluated on the same 90 % carbon capture rate.

Table 2: Main technical and environmental performance indicators for super-critical power plants

Plant indicator	Units	Case 1.1	Case 1.2	Case 1.3
Coal flowrate	t/h	165.00	208.50	199.13
Coal lower calorific value	MJ/kg	25.17		
Coal thermal energy (A)	MW_{th}	1,153.62	1,457.76	1,392.24
Gross power output (B)	MW_e	528.90	569.05	596.81
Ancillary consumption (C)	MW_e	28.90	69.05	96.81
Net power output (D = B - C)	MW_e	500.00	500.00	500.00
Net electrical efficiency (D/A * 100)	%	43.34	34.30	35.92
CO_2 capture rate	%	0.00	90.00	90.00
Specific CO_2 specific emissions	kg/MWh	800.61	89.60	77.05

As can be noticed, the energy penalty for post-combustion CO_2 capture is about 7.4 - 9 net efficiency percentage points compared to the case without carbon capture. The calcium looping system has better performances than MDEA-based gas-liquid absorption system in post-combustion CO_2 capture by about 1.6 net efficiency percentage points due to the high temperature heat recovery potential (as presented above).

3.2 Integrated gasification combined cycle power plants

The following coal-based IGCC power plants using a Shell entrained-flow gasifier and a Mitsubishi Hitachi Power Systems M701G2 gas turbine were evaluated: Case 2.1 - IGCC power plant without carbon capture; Case 2.2 - IGCC power plant with pre-combustion CO_2 capture using a MDEA-based gas-liquid absorption system; Case 2.3 - IGCC power plant with pre-combustion CO_2 capture using a calcium looping system.
A conventional state-of-the-art IGCC plant without carbon capture was considered as benchmark (IEAGHG, 2003). Table 3 presents the main performance indicators for IGCC power plants with / without carbon capture. All pre-combustion CO_2 capture cases have been evaluated on the same 90 % carbon capture rate.

Table 3: Main technical and environmental performance indicators for IGCC power plants

Plant indicator	Units	Case 2.1	Case 2.2	Case 2.3
Coal flowrate	t/h	151.00	166.80	222.00
Coal lower calorific value	MJ/kg	25.17		
Coal thermal energy (A)	MW_{th}	1,055.74	1,166.21	1,552.15
Gross power output (B)	MW_e	560.61	535.88	716.25
Ancillary consumption (C)	MW_e	76.25	108.91	156.18
Net power output (D = B - C)	MW_e	484.36	426.97	560.07
Net electrical efficiency (D/A * 100)	%	45.87	36.61	36.08
CO_2 capture rate	%	0.00	90.00	90.00
Specific CO_2 specific emissions	kg/MWh	760.25	85.48	83.02

The CO_2 capture energy penalty for pre-combustion CO_2 capture cases is about 9.2 - 9.8 net efficiency percentage points. The MDEA-based gas-liquid absorption system exhibits slightly higher net electrical efficiency in comparison to the calcium looping system by about 0.5 net efficiency percentage points due to higher CO_2 partial pressure in the syngas. As a conclusion, the MDEA-based gas-liquid absorption system performs slightly better than the calcium looping system for pre-combustion CO_2 capture in IGCC plants.

The IGCC plants with pre-combustion CO_2 capture have the particular advantage of the poly-generation capability of various totally and partially decarbonised energy carriers/chemicals such as hydrogen, methanol, synthetic natural gas, Fischer-Tropsch fuels. In a flexible operational scenario, the gasification plant with pre-combustion capture can co-produce for instance hydrogen and electricity with the ability to switch generated energy vector according to time demands from the grid. This flexible operational scenario has significant energy and cost-saving benefits e.g. overall energy efficiency in the range of 40 - 45 % (similar to non-capture systems), lower specific CO_2 emissions and better utilization of capital investment (Cormos et al., 2018).

3.3 Cement plants

The following cement plants were evaluated: Case 3.1 - Cement plant without carbon capture; Case 3.2 - Cement plant with post-combustion CO_2 capture using a MDEA-based gas-liquid absorption system; Case 3.3 - Cement plant with post-combustion CO_2 capture using a calcium looping system.

A state-of-the-art cement production plant without carbon capture with an output of 1 Mt/y was considered as benchmark case (IEAGHG, 2008). To cover the heat and power requirements for the carbon capture units (both Cases 3.2 and 3.3) a coal-based system was considered. This system will generate additional electricity (after the ancillary consumptions were covered) to be sent to the grid. An average emission factor of 520 kg CO_2/MWh was considered for power import/export. Table 4 presents the main performance indicators for the assessed cement production plants with/without carbon capture.

Table 4: Main technical and environmental performance indicators for cement plants

Plant indicator	Units	Case 3.1	Case 3.2	Case 3.3
Coal flowrate (for CCS designs)	t/h	-	33.50	22.10
Coal lower calorific value	MJ/kg	25.17		
Coal thermal energy (A)	MW_{th}	-	234.22	154.51
Steam turbine output	MW_e	-	54.40	58.12
Gross electric power output (B)	MW_e	-	54.40	58.12
Ancillary power consumption (C)	MW_e	16.24	34.16	42.38
Net electric power output (D = B - C)	MW_e	-	20.24	15.74
Net electrical efficiency (D/A * 100)	%	-	8.64	10.18
CO_2 capture rate	%	0.00	90.00	90.00
CO_2 specific emissions (on-site)	kg/t cement	728.42	135.78	120.74
CO_2 specific emissions (power export)	kg/t cement	42.02	-79.93	-62.35
CO_2 specific emissions (total)	kg/t cement	770.44	55.85	58.39
CO_2 captured	kg/t cement	0.00	1,214.17	962.20

As can be noticed, the integration of carbon capture step within the cement production significantly reduces the specific CO_2 emissions by about 92 % (56 - 58 vs. 770 kg/t). Calcium looping system has important advantages over MDEA-based gas-liquid absorption system: a lower energy penalty for CO_2 capture as well as the possible integration of spent sorbent within the cement plant with beneficial techno-economic results.

3.4 Integrated steel mills

The following steel mills were evaluated: Case 4.1 - Integrated steel mill without carbon capture; Case 4.2 - Integrated steel mill with post-combustion CO_2 capture using a MDEA-based gas-liquid absorption system; Case 4.3 - Integrated steel mill with post-combustion CO_2 capture using a calcium looping system.

A state-of-the-art integrated steel mill without carbon capture with an output of 4 Mt hot rolled coil (HRC) per year was considered as benchmark case (IEAGHG, 2013). The integrated steel mill cases were designed to be self-sufficient in term of electricity and heat; the natural gas was considered as an auxiliary fuel for covering the energy duty only when internal steel mill off-gases are not enough (Chisalita et al., 2019). The carbon capture designs are considering CO_2 capture (with a capture rate of 90 %) from the steel plant sub-systems main responsible of carbon emissions: steam plant, hot stoves, lime kilns and coke ovens. Table 5 presents the main performance indicators for the assessed integrated steel mill with/without carbon capture.

Table 5: Main technical and environmental performance indicators for integrated steel mills

Plant indicator	Units	Case 4.1	Case 4.2	Case 4.3
Fuel (natural gas) thermal energy (A)	MW_{th}	669.80	544.00	1,156.80
Gas turbine output	MW_e	-	202.31	91.06
Steam turbine output	MW_e	224.68	107.33	366.06
Gross electric power output (B)	MW_e	224.68	309.65	457.12
Power plant ancillary consumption(C)	MW_e	9.68	1.68	132.65
Net power output (D = B - C)	MW_e	215.00	307.97	324.47
Net power efficiency (D/A * 100)	%	32.10	56.61	28.04
Carbon capture rate (for captive power plant)	%	0.00	0.00	90.00
Power plant specific CO_2 emissions per MWh	kg/MWh	2,455.42	370.02	242.32
Power plant specific CO_2 emissions per t HRC	kg/t HRC	980.48	229.50	166.10
CO_2 capture rate (for CO_2 capture unit)	%	0.00	90.00	90.00
Specific CO_2 emissions (overall steel plant)	kg/t HRC	2,092.50	833.55	640.00
Captured CO_2 per t HRC	kg/t HRC	0.00	1,615.80	1,495.20

As can be noticed, the evaluated CO_2 capture scenario (from steam plant, hot stoves, lime kilns and coke ovens) reduces the specific CO_2 emissions per ton HRC by 60 – 69 %. As in the case of cement plants, also for integrated steel mills the calcium looping system performs better that MDEA-based gas-liquid absorption system (e.g. lower specific CO_2 emissions, possibility to integrate the spent sorbent within the steel mill).

4. Conclusions

The present work evaluates the main technical and environmental performances of two reactive gas-liquid and gas-solid systems used for CO_2 capture in various energy-intensive industrial applications (power generation, metallurgy, cement). As the evaluations showed, the calcium looping method performs better than the gas-liquid absorption in various post-combustion capture configurations (combustion-based power generation, cement and steel production) showing higher energy efficiencies (e.g. 1.6 net percentage points for combustion-based power plants), lower specific CO_2 emissions (by about 14 - 24 %) and possibility (in steel and cement cases) to use the spent sorbent within process. For pre-combustion capture case (gasification-based power plants), the gas-liquid absorption performs slightly better due to higher CO_2 partial pressure.

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