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Process integration of a Calcium-looping process with a natural gas combined cycle power plant for CO_2 capture and its improvement by exhaust gas recirculation

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HIGHLIGHTS

- Exhaust gas recirculation is essential for decarbonising a NGCC by Ca-looping.
- Ca-looping incurs greater energy penalty at NGCC than at coal power plant.
- Energy penalties incurred by Ca-looping were compared to those by amine processes.
- Operating conditions of Ca-looping must be adjusted against varying CO_2 contents.
- Changes of Ca-looping operating conditions affect the NGCC performance greatly.

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ABSTRACT

In this study, it was sought to find an efficient way to integrate a Ca-looping process with a Natural Gas Combined Cycle (NGCC) power plant for its post-combustion CO_2 capture. Compared to its application to coal combustion flue gas, Ca-looping would incur augmented energy penalty when integrated with a NGCC of which the flue gas contains only 4.0 mol% CO_2. The reduced CO_2 concentration in the feed requires the carbonator to operate at a lower temperature and more solids to circulate between carbonator and calciner for keeping up the carbon capture efficiency at 90%. However, this study demonstrated that such negative effects could be alleviated greatly by implementing 40% exhaust gas recirculation to the NGCC with the CO_2 concentration in the flue gas increasing up to 6.8%. Accordingly, the resulting net power efficiency increased notably 1.6% points in comparison to its equivalent non-EGR NGCC case and it was only 0.9% points less than amine capture case. This study exhibited that exhaust gas recirculation would be crucial in decarbonising a NGCC power plant by Ca-looping.

1. Introduction

Global climate change caused by greenhouse gas emissions is the most serious environmental issue to be addressed urgently and appropriately. The European Union (EU) set out its plan to cut its greenhouse gas emissions by 80% by 2050 against the 1990 levels [1]. Carbon dioxide accounted for around 80% of the total anthropogenic greenhouse gases and its emission amounted to approximately 35 billion tons per annum in 2011 [2]. Therefore, it is crucial to curtail the CO_2 emission substantially in order to meet the target to limit global warming well below 2 °C above the pre-industrial levels agreed in 2015 Paris Agreement.

In particular, the CO_2 emission resulting from fossil fuel combustion for power generation accounts for around 40% of the total anthropogenic CO_2 emission [3]. Moreover, it is likely to see global electricity demand increase substantially up to 34,290 TWh in 2030 from 19,756 TWh in 2009. It is expected that 21% of the total electricity production will still rely on natural gas by 2030 according to the IEA report. Therefore, it is necessary to develop the most efficient carbon capture process applicable to natural gas-fired power plants as well as coal-fired power plants.

For large-scale post-combustion CO_2 capture, chemical solvent processes represented by amine processes are regarded as the most commercially feasible technology, given the fact that as of 2016 the only commercial-scale CO_2 capture plant in operation for decarbonising a power plant is the amine process in the Boundary Dam CCS project. However, integrating an amine capture plant

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with a power plant requires a great deal of low pressure steam to be extracted from the steam cycle for solvent regeneration, otherwise the extracted steam would be used for power generation in non-capture case. Such a huge energy penalty of around 8% points involved in the amine capture plant [4] on top of additional CAPEX has deterred commercialisation of carbon capture and storage so far. Therefore, it is crucial to develop an alternative capture process that must be more economical than conventional amine processes for facilitating its commercialisation.

To this end, calcium-looping (Ca-looping) process has attracted great attentions from researchers due to its potential to achieve a lower energy penalty than an amine process [5–8]. Recently a 1.7 MW scale pilot plant was constructed in la Pereda, Spain and this pilot plant has been proven to work continuously for hundreds of hours achieving 90% carbon capture efficiency [9]. The heat of reaction for regenerating the $CaCO_3$ (4.1 MJ/kg CO_2) is slightly larger than the specific heat duty of an amine process using 30 wt% aqueous monoethanolamine (MEA) solvent (3.7 MJ/kg CO_2). However, the fuel heat consumed for calcination can be partly recovered by way of generating steam, which paves a way to enable a power plant to undergo less energy penalty [10,11]. By contrast such a heat recovery is inherently not possible in case of amine capture plants operating at relatively low temperatures.

It is well known [4] that the CO_2 emission factor of a NGCC (364 kgCO_2/MWh) is less than 50% those of coal-fired power plants (800 kgCO_2/MWh). However, it is generally more challenging to capture CO_2 at a NGCC than at a coal-fired power plant since the NGCC flue gas contains only 4.0 mol% CO_2, in comparison to 15 mol% in a coal-fired power plant. This is because the energy penalty involved in CO_2 capture is by and large inversely proportional to the CO_2 concentration in the feed. To overcome the adverse effect, several researchers tried to increase the flue gas CO_2 concentration by modifying the NGCC in a way of recycling part of the flue gas to the gas cycle, i.e. Exhaust Gas Recirculation (EGR). EGR can also reduce the volumetric flowrate of the flue gas flowing to the carbon capture unit, enabling the capture plant to be designed smaller in size.

Recycling 30–45% of the flue gas to the gas cycle could increase the CO_2 concentration in a NGCC flue gas up to 7.3 vol.% [12–16] as shown in Table 1. The literatures also reported that increasing the CO_2 concentration in the feed by EGR effected reducing the reboiler duty of an amine capture process and increasing the net power efficiency. But the extents of improvement vary significantly over the sources from 0.7 to 1.3% points (see Table 1). However, all the works cited have aimed to implement the EGR to improve an amine capture plant, not a Ca-looping process.

Several studies have attempted to evaluate performance of a NGCC integrated with a Ca-looping unit [6,11,17] without looking into the effect of EGR. They concluded that a Ca-looping unit using natural $CaCO_3$ would incur a greater energy penalty than an amine capture plant, its NGCC undergoing 1.4–3.5% points lower net plant efficiency. As claimed correctly by Berstad et al. [11], a carbonator designed to capture CO_2 from a NGCC flue gas containing 4 mol% CO_2 must operate at a temperature lower than 650 °C at which it would operate for capturing CO_2 from the 15 mol% CO_2 flue gas of a coal-fired power plant. Therefore, a NGCC is likely to undergo greater energy penalty than a coal-fired power plant if the power plants are to be decarbonised by a Ca-looping unit. But the augmented energy penalty can be mitigated by EGR being able to increase the CO_2 concentration in the flue gas.

In this study, it was aimed to quantify the positive impact that the increased CO_2 concentration in the flue gas as a result of implementing 40% EGR has on the energy penalty of a NGCC power plant integrated with a Ca-looping unit.

2. Process description

2.1. NGCC power plant

An exemplary NGCC power plant was selected as Base Case of this study [4] and simulated by Honeywell UniSim R443 based on the PFD and mass and energy balances available in the DOE report. A natural gas, consisting of 93.1% methane, 3.2% ethane, 0.7% propane, 0.4% n-butane, 1.0% CO_2 and 1.6% nitrogen in molar

Table 1
Summary of past researches on NGCC decarbonisation by amine and solid-looping systems.

Sources	NGCC process	Optimal capture process	CCR (avoided) (%)	Key outcomes
[12]	Ansaldo V94.3A GT, 441 MW, 59.6%	MEA + 40% EGR: 386 MW, 50.7%	90	In capture cases, EGR increased the net power efficiency by 1.3% points. EGR increased the CO_2 concentration from 4.0 to 6.6 mol%
[13]	F-class GT 557 MW, 56.9%	Aker Clean Carbon solvent + 45% EGR: 494 MW, 50.5%	90	In capture cases, EGR increased the net power efficiency by 0.7% points. EGR increased the CO_2 concentration from 3.9 to 7.3 vol.%
[14]	GE 9351FB GT 453 MW, 58.7%	32.5 wt% MEA + 38% EGR + compression heat utilisation: 390 MW, 50.5%	90	In capture cases, the net power efficiency improved 0.8% points by EGR and additional 0.54% points by compression heat recovery. EGR increased the CO_2 concentration from 4.5 to 7.3 mol%
[11]	F-class GT 416 MW, 58.1%	1) 30wt% MEA: 354 MW, 49.5% 2) Ca-looping: 525 MW, 48.1%	90–91	Heat recovery from the solid streams is essential
[17]	F-class GT 416 MW, 58.1%	1) Natural $CaCO_3$: 495 MW, 51.0% 2) Dolomite: 505 MW, 51.3% 3) Synthetic CaO: 487 MW, 53.1%	92–93	Improving the solid capacity and stability reduced the energy penalty. Greater power generation from the heat recovered at solid-looping is achievable by supercritical steam cycle
[28]	GE 9371FB GT 439 MW, 58.5%	Advanced 30wt% MEA + CO_2 Rankine cycle: 394 MW, 52.4%	90	Lean vapour recompression increased the net power efficiency by 0.9% points. CO_2 Rankine cycle increased it by 1.6% points
[15]	GE 9FB GT 442 MW, 58.3%	Advanced 30wt% MEA + 40% EGR: 390 MW, 50.7%	90	Absorber intercooling and lean vapour compression increased the net power efficiency by 0.3% points. EGR increased the net power efficiency by 0.9% points. EGR increased the CO_2 concentration from 4.2 to 7.3 mol%
[16]	F-class GT 416 MW, 58.1%	NGS(Novel Generic Solvent) + 40% EGR: 354 MW, 51.4%	90	Compared to MEA, NGS increased the net plant efficiency by 1% point. In capture cases, 40% EGR increased the net plant efficiency by 1% point. EGR increased the CO_2 concentration from 4.04 to 6.91 vol.%
[6]	M701G2 GT 495 MW	1) Ca-looping: 602 MW, 49.2% 2) MDEA: 446 MW, 52.7%	98 90	While Ca-looping incurred greater energy penalty than MDEA, it had better economic and environmental potential

All net power efficiencies are calculated on the basis of the fuel LHV.

percentage, is fed to a gas cycle equipped with an advanced F class gas turbine at 4380 kmol/h and 31 bara. It combusts with 109,323 kmol/h compressed air at a combustion chamber at 20 bara. The gas cycle was predicted to generate the power of 375.5 MW_e. The operating conditions of the gas cycle were determined so that the pressure ratio was 18.5 and the combustion gas flowing to the gas turbine was at 1365 °C.

The flue gas leaving the gas turbine at 628 °C passes through a Heat Recovery Steam Generator (HRSG) to produce superheated steams at three pressure levels. Each superheated steam is connected to its associated steam turbine for generating 203.3 MW_e electricity in total. After releasing the heat, the flue gas containing 4.0 mol% CO_2 is vented to the atmosphere.

In the steam cycle, boiler feed water (BFW) leaving a condenser is pressurised by a condensate pump and subsequently preheated in the HRSG. The preheated BFW is split into three streams and then two of them are pressurised further up to pre-set high pressure (HP) and intermediate pressure (IP) by two pumps. The three BFWs are preheated, boiled and superheated inside the HRSG by recovering heat from the flue gas. The HP steam at 167 bar and 560 °C expands at a high pressure turbine (HPT). After expansion at the turbine, the exhausted steam returns to the HRSG for reheating and then combined with the IP steam from the HRSG. Subsequently, the IP steam at 25 bar and 560 °C expands at the intermediate pressure turbine (IPT). The exhaust steam leaving the IPT is combined with the low pressure (LP) steam from the HRSG. The LP steam at 5 bar and 330 °C enters a low pressure turbine (LPT). The exhaust steam is sent to the condenser and a condensate is pressured by the condensate pump to complete the steam cycle.

2.2. Calcium-looping unit

2.2.1. Determination of carbonation temperature

A Ca-looping CO_2 capture unit consists of two fluidized reactors; a carbonator removing CO_2 from a flue gas using CaO and a calciner decomposing $CaCO_3$ into CaO and CO_2 for producing a high purity CO_2. Due to thermodynamic limitation of chemical reaction of CaO with CO_2, the carbonation temperature is usually set at 650 °C for 90% capture in case of 15 mol% CO_2 flue gases of coal-fired power plants [17–20]. The carbonation temperature must be lower than calcination temperature (950 °C). However the carbonation temperature must be chosen as closely to the calcination temperature as possible to save the energy spent for heating up the circulating solids in a calciner. In other words, carbonation reaction could take place at a temperature lower than 650 °C but it would not be recommended to do so due to more fuel being spent as sensible heat simply for heating up the solids on top of required endothermic heat of calcination reaction. Similarly, Abanades et al. [21] attempted to reduce the sensible heat by decreasing the calcination temperature rather than increasing the carbonation temperature. To this end, the CO_2 partial pressure in the calciner needs to be lowered, either operating the calciner in vacuum or flowing steam instead of CO_2 at the expense of additional operation costs. However the maximum temperature of a carbonator is limited by the CO_2 partial pressure in a flue gas. In other words, the state of solid phase (CaO or $CaCO_3$) is more or less governed by chemical reaction equilibrium which is a function of temperature and CO_2 partial pressure as follows [18].

$$f_e = \frac{10^{(7.079-8303/T)}}{p_{total}} \tag{1}$$

where f_e is CO_2 molar fraction at equilibrium; T is carbonation temperature, K; p_{total} is total pressure, atm.

Once f_e is calculated at given temperature and CO_2 partial pressure, an equilibrium-based carbon capture efficiency, E_{carb_eq}, can be estimated by Eq. (2).

$$E_{carb\_eq} = \frac{f_0 - f_e}{f_0} \tag{2}$$

where f_0 is CO_2 molar fraction in the gas feed.

Fig. 1 shows varying carbonation temperatures for achieving 90% E_{carb_eq} at different CO_2 mole fractions in the gas feed. The equilibrium-based carbonation temperature decreases from 660 °C at the CO_2 molar fraction of 0.15 (coal-fired power plant) to 605 °C at 0.04 CO_2 (NGCC). It implies that a Ca-looping process is likely to incur greater energy penalty when integrated with a NGCC due to greater difference of temperature between the two reactors. Drawbacks brought in by the lower carbonator temperature are twofold. The CO_2-depleted flue gas leaving the carbonator is at a lower temperature, resulting in its associated HRSG/steam cycle forced to operate less efficiently. More importantly, the solid stream flowing from carbonator to calciner requires more fuel to be consumed to heat solids up to the calcination temperature.

It is possible to alleviate such drawbacks inherent to the Ca-looping integrated with a NGCC by introducing a concept of EGR to the NGCC. Recycle of 40% flue gas to gas cycle can increase the CO_2 mole fraction in the flue gas up to 0.068. At the CO_2 mole fraction of 0.068, as shown in Fig. 1, the equilibrium carbonation temperature is 626 °C, 21 °C up from the non-EGR NGCC case. In other words, the carbonator can operate at a higher temperature, even though its temperature is still lower than 660 °C in case of a coal-fired power plant.

To achieve 90% carbon capture efficiency in practice, the equilibrium-based carbon capture efficiency, E_{carb_eq}, must be well over 90%. This is because actual carbon capture efficiency, E_{carb}, must be lower than the E_{carb_eq} due to another limitation imposed by the reaction rate. In this study, the carbonation temperatures were determined as 580 °C and 605 °C for non-EGR NGCC and EGR NGCC, respectively, so that the E_{carb_eq} could be around 94%. Calcination temperature was set as 950 °C and its conversion rate was assumed 100% for all cases [20].

2.2.2. Determination of F_R/F_{CO2}, F_0/F_{CO2} and solid inventory

In designing a carbonator, the actual carbon capture efficiency, E_{carb}, is determined by three operating parameters; molar flowrate ratio of circulating solids to CO_2 in the feed (F_R/F_{CO2}), molar flowrate ratio of solid purge (or make-up) to CO_2 in the feed (F_0/F_{CO2}) and solid inventory in the carbonator. Various sets of

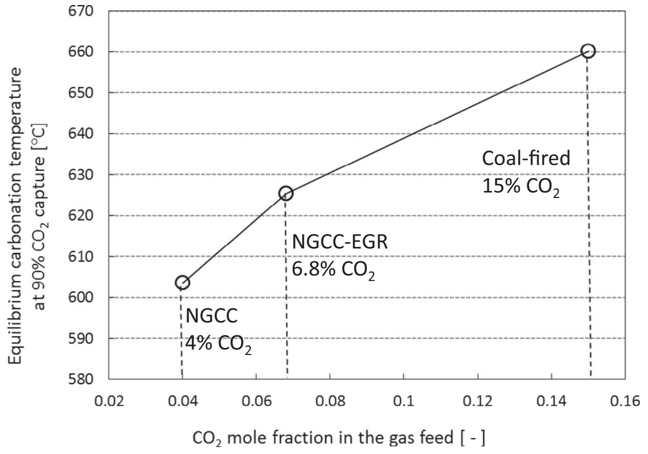

Fig. 1. Effect of the CO_2 mole fraction in the gas feed on the equilibrium-based carbonation temperature at 90% CO_2 capture.

the three parameters can be found for 90% capture efficiency given the carbonation temperature and the CO_2 mole fraction in the feed. The detailed mathematical models and algorithms were referred to other literatures [18,19,22].

Different sets of F_R/F_{CO2} and F_0/F_{CO2} were obtained to achieve 0.9 E_{carb} (90% CO_2 capture efficiency) with the solid inventory fixed as 400 kg/MW. They are presented in Fig. 2 for two cases that differ in CO_2 mole fraction in the feed and carbonation temperature. As observed clearly in Fig. 2, the F_R/F_{CO2} must be larger for the non-EGR NGCC than for the 40% EGR NGCC. This can be explained by difference of the carbonation reaction rates.

Fig. 3 shows carbonation reaction rates at different CO_2 mole fractions in the feed gas at the condition of 90% CO_2 capture efficiency. The mathematical model used for estimating the CO_2 capture efficiency of a carbonator involves a reaction rate equation, which is defined as [18]

$$r_{ave} = k_s S_{ave}(C_{CO2,0} - C_{CO2,e}) \tag{3}$$

where $C_{CO2,0}$ is CO_2 concentration in the carbonator inlet, mol/m^3; $C_{CO2,e}$ is CO_2 concentration at equilibrium, mol/m^3, determined by Eq. (1); k_s is kinetic constant, m^4/mol/s; S_{ave} is maximum average reaction surface, 1/m.

Although the values of the E_{carb_eq} are similar for all cases, the absolute difference of $C_{CO2,0}$ and $C_{CO2,e}$ becomes large with increasing CO_2 mole fraction in the feed. According to Eq. (3), the higher CO_2 mole fraction in the feed, the greater the reaction rate becomes. The k_s was assumed constant at 4×10^{-10} m^4/mol/s regardless of temperature and the S_{ave} increases only moderately with increasing CO_2 mole fraction in the feed. Therefore, the reaction rate was estimated to increase with increasing CO_2 mole fraction in the feed, mainly due to the effect of the $(C_{CO2,0} - C_{CO2,e})$ term. This can be ascertained by looking at the values of $r/(C_{CO2,0} - C_{CO2,e})$ that are almost constant over the range of CO_2 mole fraction in the feed as shown in Fig. 3. This can explain why the F_R/F_{CO2} is far greater in the non-EGR NGCC case than that in the EGR NGCC case, in particular in the region of very low F_0/F_{CO2} as shown in Fig. 2. It should be noted that, in the very low F_0/F_{CO2} region in which the kinetic effect is dominant, significant amount of the solids leaving the carbonator are still in the form of CaO. By contrast the CaO entering the carbonator are almost fully converted to $CaCO_3$ when leaving the carbonator in the high F_0/F_{CO2} region. Therefore the kinetic effect cannot be observed in the region of high F_0/F_{CO2}, resulting in almost identical F_R/F_{CO2} for the two cases.

Among the various sets of F_R/F_{CO2} and F_0/F_{CO2} giving the targeted 90% capture efficiency in Fig. 2, the F_0/F_{CO2} of 0.1 was chosen in this study. This is because the amount of CaO purge (and fresh $CaCO_3$ make-up) must be minimised, given the fact that even 0.1 F_0/F_{CO2} is not a little in quantity, amounting to 26 tons of CaO per hour in case of the commercial NGCC power plant. Moreover, Fig. 2 shows a trend of the F_R/F_{CO2} values increasing rapidly as the F_0/F_{CO2} decreases less than 0.1.

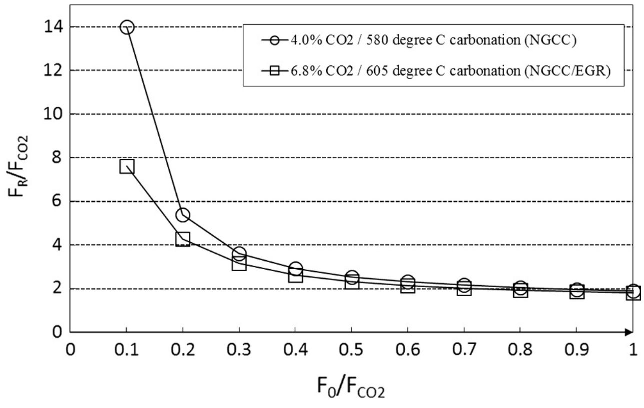

Fig. 2. Correlation of F_R/F_{CO2} and F_0/F_{CO2} for 90% CO_2 capture at the solid inventory of 400 kg/MW.

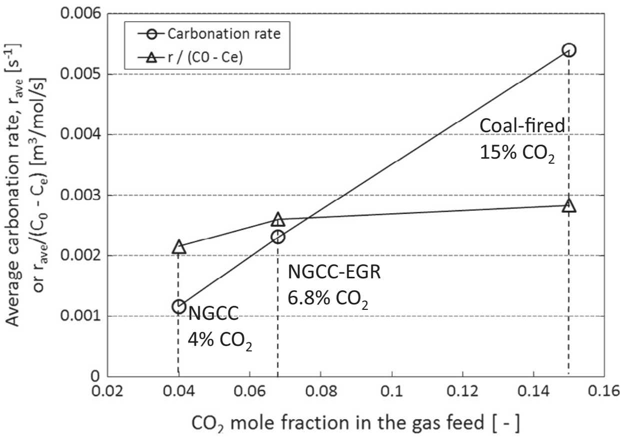

Fig. 3. Effect of the CO_2 mole fraction in the gas feed on the average carbonation rate at F_0/F_{CO2} = 0.1 and 90% CO_2 capture.

As presented in Table 2, the required F_R/F_{CO2} decreases almost half by increasing the CO_2 mole fraction in the feed from 4.0 to 6.8 mol%.

2.3. Case studies

In case of decarbonising a coal-fired power plant, there have been several literatures reporting that a Ca-looping unit would be more energy-efficient than a convention amine process [23,24]. However, it is likely that Ca-looping CO_2 capture will incur greater energy penalty when applied to a NGCC. This is due to the decreased carbonator temperature and increased solid circulation rate, both of which would result in greater fuel consumption for calcination. To evaluate if Ca-looping is worth investigating further as a promising alternative for decarbonising a NGCC, it is essential to compare the energy penalties between Ca-looping capture and conventional amine capture. An exemplary NGCC power plant integrated with an amine process using 30 wt% aqueous MEA solvent was designed and simulated for the purpose of the comparison, based on the same DOE reference [4].

Below are the list of all the cases investigated in this study along with figures depicting the overall process flow.

- Base case: NGCC reference plant
- Case 1: non-EGR NGCC + MEA absorption unit, Fig. 4(a)
- Case 2: 40% EGR NGCC + MEA absorption unit, Fig. 4(b)
- Case 3: non-EGR NGCC + Ca-looping unit, Fig. 4(c)
- Case 4: 40% EGR NGCC + Ca-looping unit, Fig. 4(d)

Table 2
Operating parameters of a carbonator.

Parameter	0.040 CO_2 (NGCC)	0.068 CO_2 (EGR-NGCC)
Temperature	580 °C	605 °C
F_R/F_{CO2}	14	7.6
F_0/F_{CO2}	0.1	
Solid inventory	400 kg/MW	
CO_2 capture efficiency	90%	

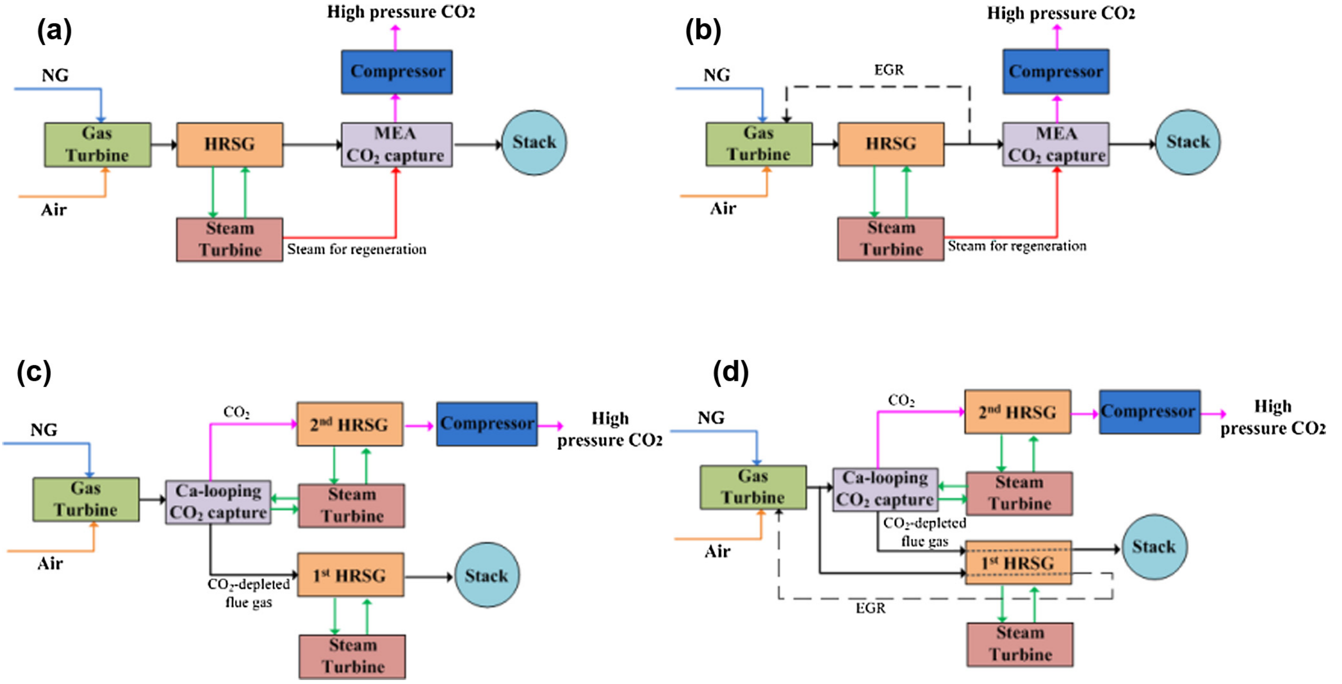

Fig. 4. Block flow diagram of a NGCC integrated with a CO_2 capture unit: (a) non-EGR NGCC + MEA, (b) EGR NGCC + MEA, (c) non-EGR NGCC + Ca-looping and (d) EGR NGCC + Ca-looping.

3. Process simulation

3.1. Simulation basis

All the gas streams and their associated unit operations except for amine processes were simulated with Peng-Robinson EOS while the steam cycle was based on ASME-Steam package. Amine package/Li-Mather method was taken for amine process simulation in Cases 1 and 2. To incorporate calcium oxide and calcium carbonate in UniSim, hypothetical compounds were created, of which the thermodynamic properties, such as heat of formation and temperature-dependent heat capacity, were assigned manually as shown in Table 3. The CO_2 compression train was also simulated with Peng-Robinson EOS. Any heat losses were not taken into account in the simulations of all cases, assuming that the processes would behave adiabatically. Therefore, our simulations of Base Case and Case 1 predicted consistently greater net power efficiencies than the DOE references by 1.5–1.9% points.

For both primary and secondary steam cycles, the adiabatic turbine efficiencies were set identically as 85.5% for HPT and 91.5% IPT. The adiabatic turbine efficiency of LPTs were determined by allowing the exhaust gas to contain 5% liquid fraction in it. As a result, they were consistently in the range of 86–88% for all cases.

3.2. Simulation results

All the simulation results are summarised in Table 4.

3.2.1. NGCCs with MEA absorption CO_2 capture (Cases 1 and 2)

In Case 1 (amine capture at the non-EGR NGCC), the net power efficiency was reduced by 7.7% points against Base Case. Around 54% steam had to be extracted of the IP/LP crossover in order to supply the reboiler heat at the amine process for 90% carbon capture efficiency.

Conflicting results can be found among the literatures on the effect of an EGR on the net plant efficiency at the amine process as shown in Table 1. It is well known that the effect of the absorption rate on the solvent CO_2 loading is dominant in the absorber while CO_2 reaches its equilibrium loading more quickly in the stripper [25]. Therefore, the higher CO_2 mole fraction the feed has, the easier the amine solvent reaches the equilibrium rich loading of around 0.5 in the CO_2 absorber. In this respect, the specific heat duty at the CO_2 removal MEA absorption unit may be reduced in the EGR NGCC due to higher rich loading achievable by greater CO_2 driving force, given the same size of a CO_2 absorber. In other words, such a kinetic limitation can be overcome by adjusting the absorber size. In this study, it was assumed that the CO_2 absorber was so large that the amine solvents could almost reach the equilibrium rich loading in the CO_2 absorber without having to have the EGR implemented. Therefore, the energy penalty incurred by steam extraction was almost identical in Cases 1 and 2 of this study. However, power consumptions of the blower compressing the flue gas by 10 kPa to overcome the pressure drop along the absorber are different between the two cases. This is due to huge difference of volumetric flowrates of the flue gas flowing to the

Table 3
Properties of CaO and $CaCO_3$ required to create the hypo-components in UniSim [29].

Hypo-component	Molecular weight	Density [kg/m^3]	Standard heat of formation [kcal/mol] at 25 °C	Heat Capacity [cal/mol K] $C_p = a + bT + cT^2 + dT^{-2,}$ T in K			
				a	b	c	d
CaO	56.08	3320	−151.7	10	0.00484	0	−108,000
$CaCO_3$	100.09	2711	−289.5	19.68	0.01189	0	−307,600

Table 4
Simulation results of Base Case and Cases 1–4.

Case		Base case	Case 1	Case 2	Case 3	Case 4
Process description	Unit	NGCC	NGCC + MEA	NGCC/EGR + MEA	NGCC + Ca-looping	NGCC/EGR + Ca-looping
Heat input to gas cycle (LHV)	MW_{th}	995.2	995.2	995.2	995.2	995.2
Heat input to calciner (LHV)	MW_{th}	0	0	0	773.5	535.9
Gas turbine power (efficiency on gas cycle fuel basis)	MW_e (%)	375.5 (37.7)	375.5 (37.7)	369.8 (37.2)	375.5 (37.7)	369.8 (37.2)
Primary steam turbine power (efficiency on gas cycle fuel basis)	MW_e (%)	203.3 (20.4)	151.9 (15.3)	156.5 (15.7)	166.1 (16.7)	188.9 (19.0)
HP turbine	MW_e	48.3	48.3	49.4	38.5	44.9
IP turbine	MW_e	59.8	59.8	61.1	48.7	55.6
LP turbine	MW_e	95.2	43.8	46.0	78.9	88.4
Secondary steam turbine power (efficiency on calciner fuel basis)	MW_e (%)	–	–	–	409.1 (52.9)	277.7 (51.8)
HP turbine	MW_e	–	–	–	99.3	67.4
IP turbine	MW_e	–	–	–	138.9	94.3
LP turbine	MW_e	–	–	–	170.9	116.0
Total power generation	MW_e	578.8	527.4	526.3	950.7	836.4
Auxiliary power in primary steam cycle and its cooling system	MW_e	6.7	9.9	9.9	5.5	6.2
Auxiliary power in secondary steam cycle and its cooling system	MW_e	–	–	–	13.5	9.2
CO_2 compression	MW_e	–	13.5	13.3	37.1	31.6
Air separation unit	MW_e	–	–	–	46.9	32.5
Auxiliary power in capture unit	MW_e	–	9.1	5.4	9.1	5.4
Transformer loss	MW_e	1.8	1.6	1.6	2.9	2.5
Miscellaneous	MW_e	1.2	1.2	1.2	1.2	1.2
Total auxiliaries	MW_e	9.7	35.3	31.4	116.2	88.7
Net power	MW_e	569.1	492.1	494.9	834.5	747.7
Net power efficiency (LHV)	%	57.2	49.4	49.7	47.2	48.8
Specific power consumption	$MJ_e/kg\ CO_2$	–	1.51	1.47	1.96	1.63
CO_2 purity in the CO_2 product	%	–	99.7	99.7	92.4	93.7

amine process between the two cases. As a result, implementing the 40% EGR could increase the net power efficiency by 0.3% points.

It is also worth noting that the HRSG in amine capture cases cannot operate as efficiently as one in Base Case due to the significant steam extraction from the steam cycle. The cold flue gas leaving the HRSG was at 112 °C in Base Case while it was at 148 °C in the two amine capture cases. This is because less condensate was available to recover the heat of the flue gas in the low temperature region inside the HRSG since almost half of the circulating BFW was already condensed in the stripper reboiler. The DOE reference our amine capture simulations were based on also reported less efficient use of the HRSG in amine capture case, similarly to this study [4]. As a result, the specific energy consumption was around 1.5 $MJ_e/kg\ CO_2$, slightly higher than 1.4 $MJ_e/kg\ CO_2$ in case of coal-fired power plants [26].

3.2.2. Case 3: Non-EGR NGCC + Ca-looping CO_2 capture

Schematic diagrams of the two Ca-looping cases are shown in Fig. 5.

Since carbonation reaction is exothermic, the heat of reaction must be removed to maintain the carbonator temperature constant at a set point. In this study, the exothermic heat of reaction is removed by the hot BFW flowing through the carbonator and recovered as a saturated steam leaving it at 374 °C and 220 bar.

The CO_2-depleted flue gas leaving the carbonator enters a primary HRSG to recover the heat and then is vented through a stack at 110 °C. The solid stream leaving the carbonator is sent to a calciner for regeneration. In the calciner, calcination reaction takes place at 950 °C for converting $CaCO_3$ back into CaO and CO_2. The hot CO_2 stream leaving the calciner passes through a secondary HRSG for heat recovery and then sent to a multistage CO_2 compression train in which the CO_2 product is compressed and subsequently pressurised up to 150 bara. The calcined solids are recycled back to the carbonator. To supply the heat required for the endothermic reaction taking place in the calciner, additional natural gas is fed to the calciner and combusted with 95 mol% purity oxygen. The power consumption at a cryogenic air separation unit for producing the 95 mol% oxygen was set as 200 kWh/ton oxygen [22]. Since the CaO originating from natural $CaCO_3$ loses its activity very quickly over the cycles, part of the circulating solids, its molar flowrate denoted by F_0 in Fig. 5, must be removed from the solid cycle as a purge. To compensate for the solid purge, the same amount of fresh $CaCO_3$ must be replenished to maintain the targeted molar flowrate of circulating solids around the carbonator (F_R).

In the Ca-looping cases, energy penalty involved in carbon capture is attributed mainly to additional fuel consumption at the calciner. However the energy penalty can be reduced greatly by having the secondary HRSG and its dedicated steam cycle (220 bar/680 °C/680 °C), recovering heats from (i) exothermic heat of reaction at the carbonator, (ii) hot CO_2 stream leaving the calciner and (iii) hot solid stream leaving the calciner as shown in Fig. 5. For heat recovery from the hot CaO stream for superheating the steam, a solid moving bed heat exchanger equipped with steam tubes can be utilised [27].

Since the secondary HRSG is interwoven closely with the Ca-looping unit for enabling efficient heat recovery, it is very different from conventional HRSGs. For example, in primary HRSG, the heat source is only the flue gas and the heat exchanges all take place internally.

As the cold CO_2 stream leaving the secondary HRSG at 140 °C is not vented through a stack but cooled down further for the following CO_2 compression, its temperature is not subject to general stack temperature conditions. Therefore, it is possible to cool it down below a stack temperature to recover the heat further for heating up the condensate, achieving greater heat recovery.

In addition, availability of very hot heat sources, i.e. CO_2 product stream and the CaOs leaving the calciner both of which are hotter than general flue gases, enables the secondary HRSG to generate HP and IP steams at a higher temperature than general HRSGs can do. Moreover, the secondary HRSG is simpler in structure than

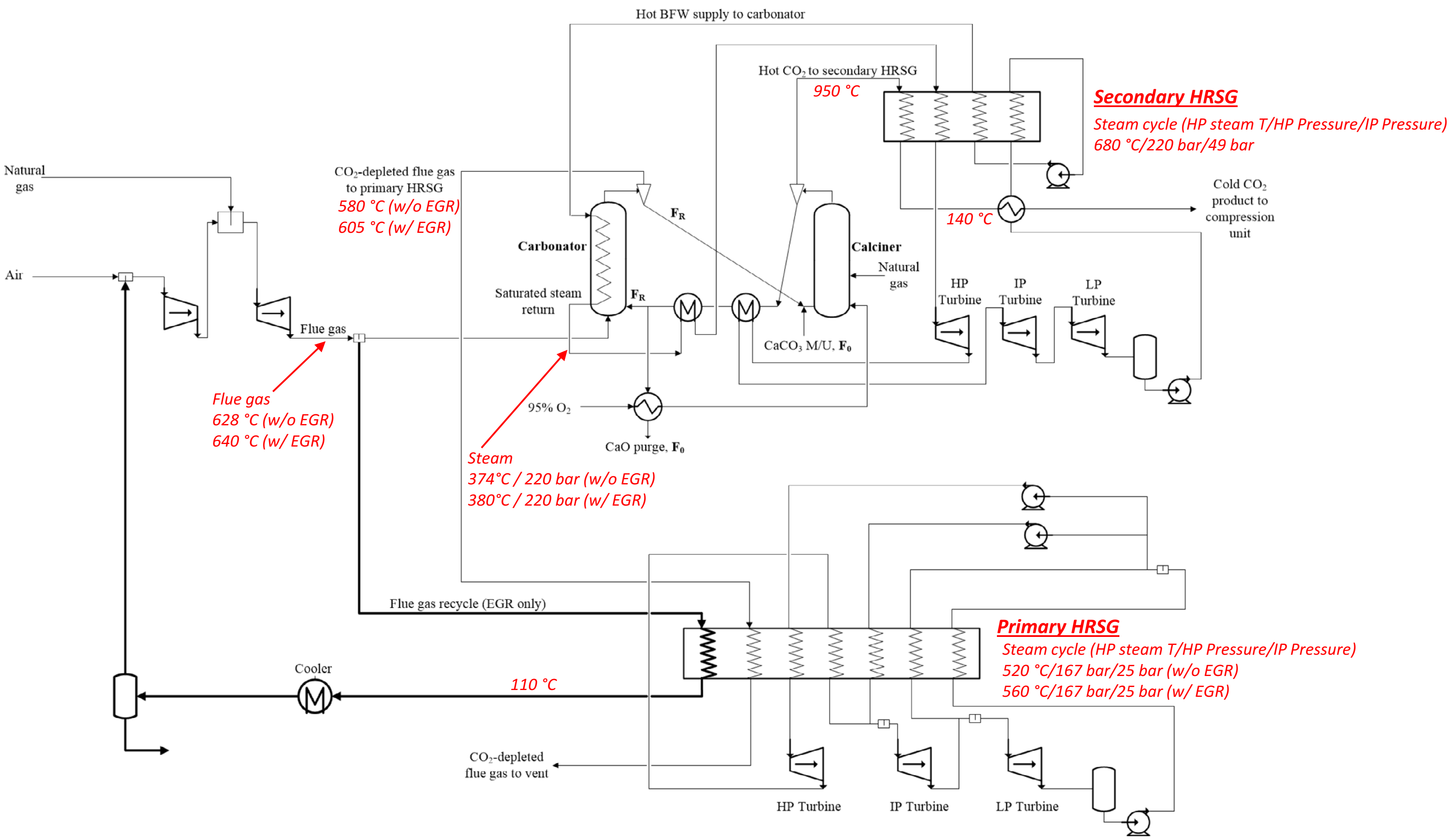

Fig. 5. Process flow diagram of a NGCC integrated with a Ca-looping unit. (Thick solid lines denote additional piping and units for EGR.)

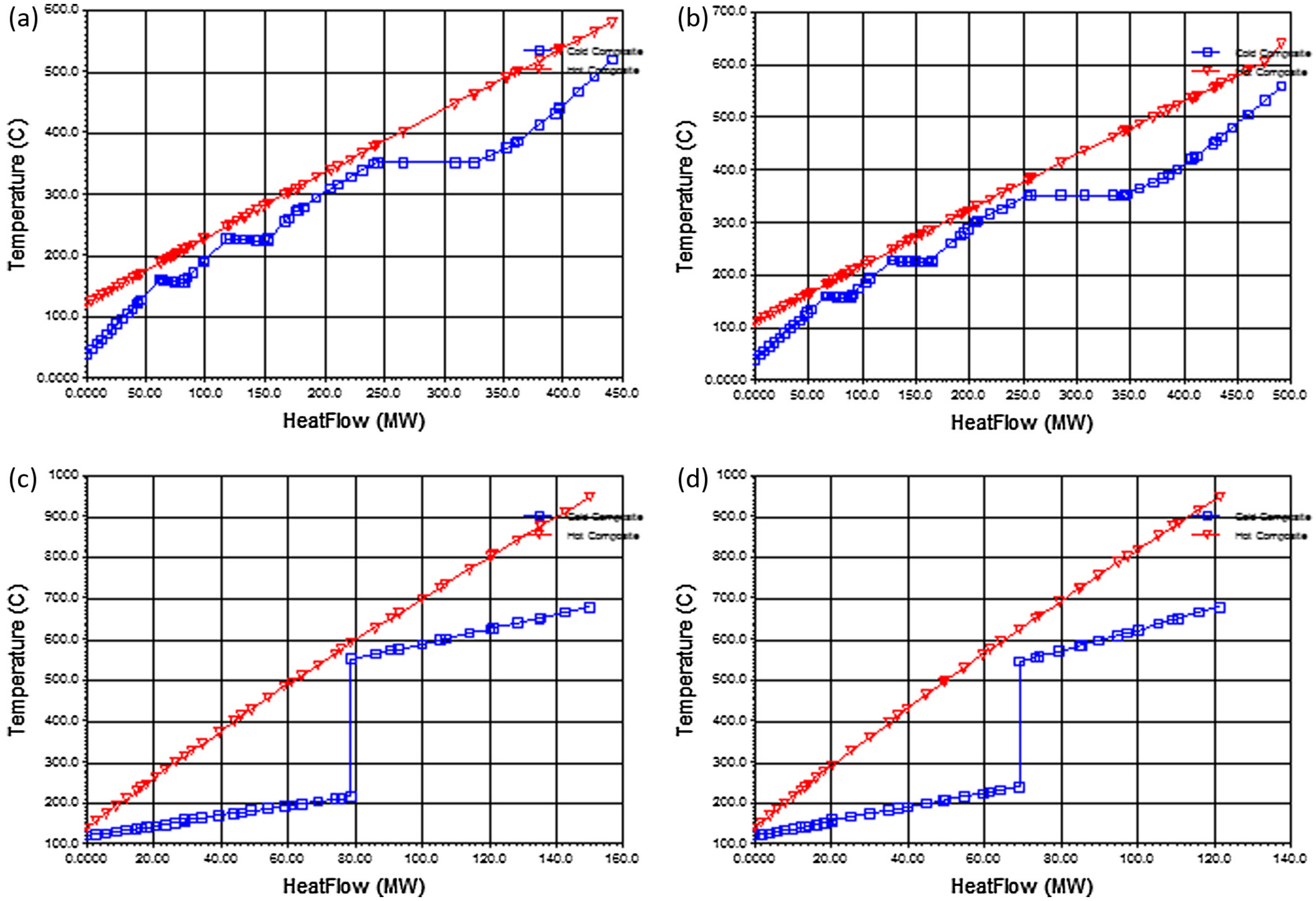

Fig. 6. Hot and cold composite curves of primary and secondary HRSGs constructed by UniSim, (a) primary HRSG at non-EGR, (b) primary HRSG at EGR, (c) secondary HRSG at non-EGR, and (d) secondary HRSG at EGR.

the primary HRSG since BFW boiling, reheating and part of superheating take place externally in the proximity of the Ca-looping unit. As a result, the steam cycle associated with the secondary HRSG could achieve a very high energy efficiency, recovering 53% out of the heat of the fuel supplied to the calciner as power. It should be noted that the natural gas fuel fed to the NGCC gas cycle also contributed partly to steam generation in the secondary HRSG through the hot CO_2 product stream. The CO_2 in the flue gas, being at 628 °C on its arrival at the Ca-looping unit, was heated up to 950 °C at the calciner and subsequently cooled down to 55 °C, well below the inlet temperature of 628 °C. By contrast, the primary HRSG and its steam cycle could not operate as efficiently as the HRSG in Base Case because the CO_2-depleted flue gas, which is the only heat source of it, is at 580 °C in marked contrast to 628 °C in Base Case. In proportion to the decrease of the flue gas temperature, the temperatures of HP and IP steams had to be adjusted to 520 °C from 560 °C in Base Case so that the two HRSGs could achieve the heat fluxes to a similar extent. Inevitably, decreasing the HP and IP temperatures results in less power being produced at the associated steam turbines, being deemed as additional energy penalty incurred by integrating a NGCC with Ca-looping. In this study, the primary and secondary HRSGs were designed so that both of them could have at least 20 °C difference at the pinch temperature. The hot and cold composite curves that UniSim generated are shown in Fig. 6.

As a result, Case 3 underwent significant reduction in the net power efficiency, achieving only 47.2% that was 2.2% points lower than its equivalent amine capture case, implying that Ca-looping would not be as energy-efficient as amine capture.

3.2.3. Case 4: 40% EGR NGCC + Ca-looping CO_2 capture

By implementing 40% EGR to the NGCC as shown in Fig. 5, additional fuel consumption at the calciner could be reduced drastically by 31% (see Table 3). This was due to (i) reduction in circulating solids, F_R and (ii) carbonator temperature increasing from 580 °C to 605 °C, both of which effected reducing the sensible heat for heating up the circulating solids. As a result, the power consumption at auxiliary units were reduced accordingly due to both oxygen consumption and CO_2 flowrate for compression decreasing.

However the amount of heat available for steam generation at the secondary HRSG is drastically reduced in Case 4, while the heats of carbonation reaction are almost identical in Cases 3 and 4. This is due to both the hot CO_2 product flowrate and the solid circulation flowrate decreasing in Case 4. To compensate for the reduced heat avail, the steam leaving the carbonator was deliberately superheated up to 380 °C, reducing its flowrate.

We can design the primary HRSG in Case 4 more efficiently than in Case 3, since two flue gases are available as heat sources for the primary HRSG in Case 4, i.e. one flowing from the gas cycle at 640 °C and the other from the carbonator at 605 °C in marked contrast to a single heat source at 580 °C in Case 3. Given the temperatures of the two flue gases, the primary HRSG can produce the HP and IP steams of the same quality as those of the Base Case HRSG. But its steam cycle cannot be as efficient as one in the Base Case due to one of the two hot streams being at a lower temperature than the flue gas temperature of 640 °C. As a result, the net power efficiency of its steam cycle was 19%, lying between Base Case and Case 3 as shown in Table 3. The hot and cold composite curves at the two HRSGs are compared with those in Case 3 in Fig. 6.

In short, the positive impacts that implementing 40% EGR to a NGCC has on operating conditions of a Ca-looping unit were

- Increasing the carbonator temperature from 580 °C to 605 °C.
- Decreasing the solid circulation rate by around 50%.

These two impacts effected the overall NGCC plant having the following positive consequences.

- Less fuel consumption at the calciner leading to lower power consumption at auxiliary units for oxygen generation and CO_2 compression.
- Enhancing the net power efficiency at primary HRSG.
- Less flue gas flowrate to the carbonator leading to less power consumption of the flue gas blower.
- Reducing the CO_2 compression power further thanks to its higher CO_2 product purity.

Case 4 benefits greatly from all the favourable impacts and consequences listed above, its net power efficiency being improved up to 48.8%, 1.6% points up from Case 3. Note that the substantial improvement can be made simply by implementing the 40% EGR to a NGCC. The net power efficiency of Case 4 is only 0.9% points less than that of Case 2. In this respect, Ca-looping can be still deemed as an alternative to amine capture in decarbonising a NGCC as well as coal-fired power plants as long as exhaust gas recirculation is implemented to a NGCC.

Meanwhile, such a high net power efficiency could be achieved only if a great amount of the fuel energy consumed in the calciner was recovered as power. As shown in Table 4, the net power efficiency of the secondary HRSG-driven steam cycle in Case 4 amounts to 52% on the basis of calcination fuel heat. Such a high energy efficiency must be challenging but is achievable with the process integration strategy proposed in this study.

4. Conclusions

It was demonstrated that, in integrating a NGCC power plant with a Ca-looping unit, exhaust gas recirculation (EGR) must be implemented to minimise the energy penalty involved in carbon capture, while the effect might be marginal in case of amine capture. The energy penalty that Ca-looping incurred in decarbonising a NGCC could be reduced by 40% EGR to such an extent that it is comparable to those of amine capture cases. Such a low energy penalty is achievable if a significant amount of the fuel heat consumed in the calciner is to be recovered as power through the heat recovery strategy proposed in this study.

Since capital cost as well as energy penalty come into play for selection of optimal capture process, it is impetuous to judge that amine capture case would be more advantageous than Ca-looping cases for the 0.9% points' difference of the net plant efficiency. Hence, subsequent study is required to assess the two capture options from a comprehensive perspective taking into account CAPEX as well as OPEX. And the process design this work presented can act as a basis of such a techno-economic study.

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