Perspective

# Making gas-CCS a commercial reality: The challenges of scaling up

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Abstract: Significant reductions in $CO_2$ emissions are required to limit the global temperature rise to 2°C. Carbon capture and storage (CCS) is a key enabling technology that can be applied to power generation and industrial processes to lower their carbon intensity. There are, however, several challenges that such a method of decarbonization poses when used in the context of natural gas (gas-CCS), especially for solvent-based (predominantly amines) post-combustion capture. These are related to: (i) the low $CO_2$ partial pressure of the exhaust gases from gas-fired power plants (~3-4%vol. $CO_2$), which substantially limits the driving force for the capture process; (ii) their high $O_2$ concentration (~12-13%vol. $O_2$), which can degrade the capture media via oxidative solvent degradation; and (iii) their high volumetric flow rates, which means large capture plants are needed. Such post-combustion gas-CCS features unavoidably lead to increased $CO_2$ capture costs. This perspective aims to summarize the key technologies used to overcome these as a priority, including supplementary firing, humidified systems, exhaust gas recirculation and selective exhaust gas recirculation. These focus on the maximum $CO_2$ levels achievable for each, as well as the electrical efficiencies attainable when the capture penalty is taken into account. Oxy-turbine cycles are also discussed as an alternative to post-combustion gas-CCS, indicating the main advantages and limitations of these systems together with the expected electrical efficiencies. Furthermore, we consider the challenges for scaling-up and deployment of these technologies at a commercial level to enable gas-CCS to play a crucial role in a low-carbon future. © 2017 The Authors. Greenhouse Gases: Science and Technology published by Society of Chemical Industry and John Wiley & Sons, Ltd.

Keywords: $CO_2$ capture; exhaust gas recirculation; gas-CCS; humidified turbine cycles, oxy-fired gas turbines; supplementary firing

## Introduction

The need to limit global temperature rise to or below 2°C to avoid negative outcomes associated with climate change requires profound cuts in $CO_2$ emission levels.[1] This is a real challenge in the current context, characterized by a continuous increase in energy demand and a large share of fossil fuels in the energy mix. Improvements in energy efficiency and wider deployment of renewables and nuclear energy have been proposed in order to help in this transition toward cleaner energy technologies.[2] However, all estimates show that fossil fuels will still play an important role in the energy mix for the next few decades.[3] Here, we present the case of natural gas, whose worldwide consumption for energy-related uses

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is expected to increase in the near future, accounting for between 40 and 67% of the total fossil fuel electricity production by 2040.[3] Despite gas-fired power plants showing the lowest carbon intensity amongst fossil fuels systems, they still emit large quantities of $CO_2$ (around 350 kg $CO_2$/MWh for a natural gas combined cycle (NGCC)).[4] In this scenario, carbon capture and storage (CCS) is widely recognized as a key enabling technology that can allow using existing fossil fuel resources, whilst achieving substantial cuts in $CO_2$ emissions.[2,3] In fact, it has been estimated that the accumulated contribution of CCS toward $CO_2$ emissions reduction from all fuel sources can be up to 14% by 2050.[2]

Capturing $CO_2$ from gas-fired power plants (gas-CCS) is challenging because of the large flows of flue gas with relatively low $CO_2$ concentration (3–4%vol.) generated in these systems, which impose high energy penalties. This is a consequence of the large excess airflows required to limit temperatures in the combustor and avoid turbine damage. Several $CO_2$ capture technologies are currently being investigated for gas-fired power plants, with post-combustion capture (PCC) using amines being the most developed so far. Amine-based $CO_2$ capture has been demonstrated commercially for coal applications at Boundary Dam, in Canada.[5] Also, a new commercial plant, Petra Nova,[6] has been built to capture $CO_2$ from a coal-fired power plant in Texas, USA, using an amine-based solvent. This facility has recently gone beyond the testing phase, becoming the largest CCS plant in operation.[6] However, the characteristics of the flue gas generated in gas-fired plants are different to those from coal-fired plants (12–15%vol. $CO_2$, $\sim$3%vol. $O_2$). As discussed, low flue gas $CO_2$ concentrations of up to just 4%vol. and high $O_2$ contents ($\sim$12–13%vol.) are typical of gas-fired systems, which are known to have detrimental effects on the energy requirements of amine capture plants and on the long-term performance of the capture media, respectively.[7,8] Extensive efforts have been devoted to reducing the energy consumption of amine capture plants and decreasing the costs of $CO_2$ capture.[9–11] Moreover, numerous investigations have focused on increasing the $CO_2$ concentration in the flue gas of gas-fired systems (and thus, reducing its $O_2$ content),[8,12–19] which can improve the performance of the absorber and stripper units and reduce the size of the whole capture plant. This, in turn, can result in significant energy and cost reductions – particularly in the capital and operational expenditure (CAPEX and OPEX) – and contribute to the deployment of gas-CCS. For this purpose, modifications to existing systems, alternative processes and new configurations have been proposed, including the use of supplementary firing,[8,12–14,20,21] exhaust gas recirculation,[8,15,16,22,23] selective exhaust gas recirculation,[17,24] and humidified cycles.[8,17–19,25–28] Also, advancements have been made for the development of oxy-fired gas turbine cycles,[15,29–34] which are seen as a potential alternative to post-combustion capture systems.

This work deals with the above-mentioned post- and oxy-combustion processes coupled to gas-fired power plants for the purpose of CCS; however, pre-combustion capture options are beyond the scope of this study at present and thus not considered herein because of their expected less favorable performance and economics.[4] This perspective focuses on the state-of-the-art technologies and discusses the maximum $CO_2$ levels achievable in the flue gas sent to the capture plant for post-combustion applications, as well as the overall electrical efficiencies that can be attained in each case when the $CO_2$ capture penalty is considered. This study also highlights the main characteristics and challenges of such systems relevant for the scale-up and deployment of gas-CCS at commercial scale.

## Post-combustion $CO_2$ capture in gas-fired systems

As indicated earlier, the wide-scale commercial deployment of post-combustion gas-CCS technologies requires reducing the energy penalty and costs of $CO_2$ capture. This can be attained by a combined increase in the flue gas $CO_2$ concentration and optimization of the capture system itself, which are now discussed in detail.

### Strategies to increase the flue gas $CO_2$ content in gas-CCS systems

### Supplementary firing

Supplementary firing has been suggested as an option to facilitate $CO_2$ capture in NGCC power plants.[8,12–14,20,21] It consists of burning additional fuel after the gas turbine using the oxygen still present in the exhaust gas as the oxidizer, as depicted in Fig. 1. The $CO_2$ content of the flue gas sent to the amine capture system is then increased, favoring the driving force for $CO_2$ capture in the absorber and reducing the heat demand in the stripper.[8,12] The oxygen content in

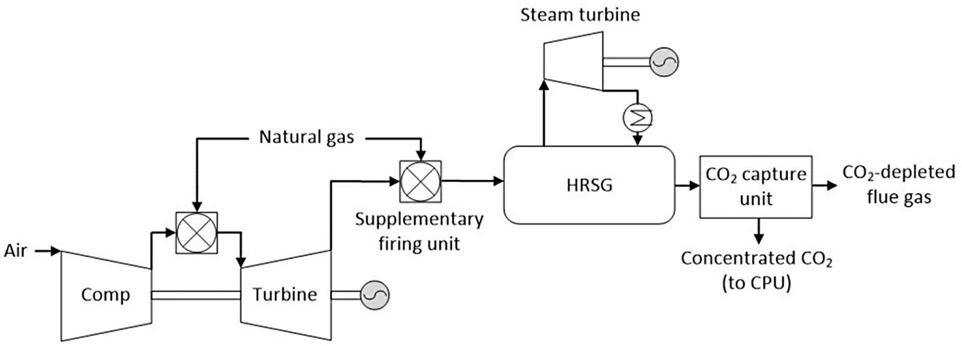

Figure 1. Schematic of the supplementary firing option for NGCC power plants with $CO_2$ capture (CPU: compression and purification unit).

the exhaust gas sent to the absorber also diminishes, leading to reduced solvent degradation.[35] Lower $NO/NO_2$ (NOx) content has also been reported.[12] A further benefit of this configuration is the possibility of using biomass instead of fossil fuels in the supplementary firing stage. This allows further $CO_2$ emission reductions since the carbon intensity of biomass is lower than that of fossil fuels, and coupled with CCS is associated with the concept of net negative emissions.[36–38] Also, additional power can be generated in the bottoming steam cycle of the heat recovery steam generator (HRSG), as the flue gas enters this section at a higher temperature. Nevertheless, the use of supplementary firing decreases the overall efficiency of the power plant, which is typically around 57–63% (all efficiencies shown in this work are LHV) for advanced unabated NGCC power plants (without supplementary firing).[39] This is because the extra fuel used in the supplementary firing stage only generates power in the steam cycle (Rankine), which is less efficient than the combined Brayton and Rankine cycles in NGCC plants, and also due to the higher temperature difference between the flue gas and the water/steam streams in the HRSG.[12] Overall efficiencies of ~43–48% have been reported for supplementary firing systems integrated with an amine $CO_2$ capture plant,[8,12,13] which is lower than that calculated for NGCC power plants with similar post-combustion capture systems and without supplementary firing.[12,13] However, it has been reported that despite the efficiency decrease, the amount of flue gas generated in a system designed to continuously operate under supplementary firing conditions is lower than that in conventional power plants for the same power output.[13] This can potentially reduce the CAPEX of $CO_2$ capture systems by allowing more compact designs.[13]

Supplementary firing was first proposed for non-$CO_2$ capture purposes[40] and it is used commercially at some NGCC power plants to produce additional energy during peak demand periods.[41] These systems have greater load flexibility, making them more competitive when energy demand increases (higher electricity price), despite the reduced efficiency. Supplementary firing has also been proposed as an option to compensate for the power loss experienced at NGCC plants when ambient temperature rises.[42] However, this technology faces several challenges, which are especially important for its deployment in NGCC plants with integrated $CO_2$ capture systems. A limitation in the configuration of Fig. 1 is the maximum temperature allowed in the HRSG, which is associated with material resistance. The maximum temperature of the flue gas entering the HRSG is usually around 800°C,[13,20] although it can be increased up to ~900°C or 1300°C if insulated casings or water-cooled furnaces are used in the HRSG, respectively.[43] This temperature restriction affects the amount of fuel that can be burned in the supplementary firing system, which limits the maximum $CO_2$ concentration that can be attained in the flue gas. This effect has been studied by Li *et al.*[8,12] who found that the $CO_2$ content can be increased from 3.9%vol. to 6.7%vol. and 8.4%vol. without and with flue gas condensation, respectively, for a supplementary combustion temperature of 1328°C – this temperature should be enough to compensate for the lower $O_2$ content in the oxidant (around 12%vol.) and ensure stable combustion.[8] These authors also studied the increase in the flue gas $CO_2$ content obtained at the expense of higher combustion temperatures until the stoichiometric oxygen limit is reached (i.e., 11.3%vol. $CO_2$ at ~1970°C)[8].

Sequential supplementary firing is an option to achieve a high flue gas $CO_2$ concentration whilst limiting the temperature in the flue gas to reasonable values (around 800–900°C). This approach was recently investigated by Gonzalez *et al.*,[13] in terms of its applicability to NGCC plants coupled with amine-based capture systems. It consists of burning fuel in several stages across the HRSG, which allows more supplementary fuel to be combusted with only moderate increases in flue gas temperatures across each firing stage. As a result, no special alloys or configurations of the HRSG are needed, and a smaller temperature difference is found in the HRSG, which improves system efficiency.[13] The results of this study indicate that up to 57% of the total fuel input can be burned in the HRSG, leading to a $CO_2$ concentration in the flue gas of 10.9%vol. with maximum temperatures in the HRSG of 820°C.[13] However, combustion may be limited in the final burners due to the low available $O_2$ content, which is $\sim$1%vol. for the ultimate firing stage in the study of Gonzalez *et al.*[13] These authors indicate this may not be a problem, since the high combustion temperatures can compensate for the low $O_2$ concentrations,[13] based on their review of Li *et al.*[8] data. Nevertheless, combustion temperatures in sequential supplementary systems are much lower than those in the conventional supplementary firing configurations analyzed by Li *et al.*[8] Therefore, the combined effects of a low $O_2$ content and a high $CO_2$ concentration in the oxidant stream in the last combustion stages of sequential supplementary firing systems should be carefully analyzed.

Another challenge for incorporating supplementary firing in NGCC systems is the decrease in overall power plant efficiency, as discussed above. The use of supercritical HRSG designs has been analyzed to compensate for such efficiency reductions.[12,13] Although the need for developing gas turbines that can operate at high exhaust gas temperatures (beyond 630°C) is negated by the use of supplementary firing configurations, there are still technological challenges for the incorporation of supercritical steam cycles in NGCC plants. Supercritical HRSGs are associated with higher costs and reduced flexibility.[12,44] Therefore, alloy materials need to be developed that can withstand cycling at a reasonable cost during the load following operation expected in these systems.[44]

Other alternative configurations have been initially explored by Li *et al.*,[12] with the objective of increasing the efficiency of supplementary firing NGCC power plants and improving system performance. This is the case of supplementary firing systems integrated with exhaust gas reheating or with exhaust gas recirculation, and the combination of supplementary firing, exhaust gas reheating and recirculation, together with a supercritical HRSG design.[12] Further advanced configurations with exhaust gas recirculation and different options for the integration of the supplementary firing NGCC and the amine capture plant can be found elsewhere.[14,20,21] However, all these configurations come at the expense of an increase in complexity and reduced flexibility of the NGCC power plant, and further techno-economic analysis is required in order to quantify the actual advantages of these systems.

## Exhaust gas recirculation

Exhaust gas recirculation (EGR) involves recycling a proportion of the exhaust gas to the compressor and mixing this stream with the combustion air, after cooling and condensing out the moisture,[15] as illustrated in Fig. 2. This cooled, recycled exhaust gas replaces a fraction of the inlet air in the working fluid that passes through the turbine, thus decreasing the flow rate and increasing the $CO_2$ concentration of the exhaust gas sent to the $CO_2$ capture plant. As a result, the energy penalty and costs associated with $CO_2$ capture from NGCC plants reduce, notably, both equipment size and reboiler duty.[15,16,22,23,45–47]

Deployment of EGR in NGCC power plants at industrial scale presents several challenges, mainly related to flame stability. From Fig. 2, it is evident that oxygen availability in the combustor will fall as the EGR ratio increases (defined as the ratio between the volume of recirculated exhaust gas and the total volume of exhaust gas), resulting in issues such as combustion instability and increased concentrations of certain species of incomplete combustion, for example CO and unburnt hydrocarbons (UHC).[45,48] Some authors have studied the effect of oxygen concentration on combustion in gas turbines under conditions characteristic of the EGR configuration. Ditaranto *et al.*[49] demonstrated flame stability can be maintained at a minimum oxygen concentration of 14%vol. at the inlet of the combustor, although high levels of CO and UHC are obtained under these conditions. Similar conclusions were achieved by ElKady *et al.*,[46] who illustrated that combustion could be maintained at $O_2$ concentrations below 4%vol. at the outlet of the

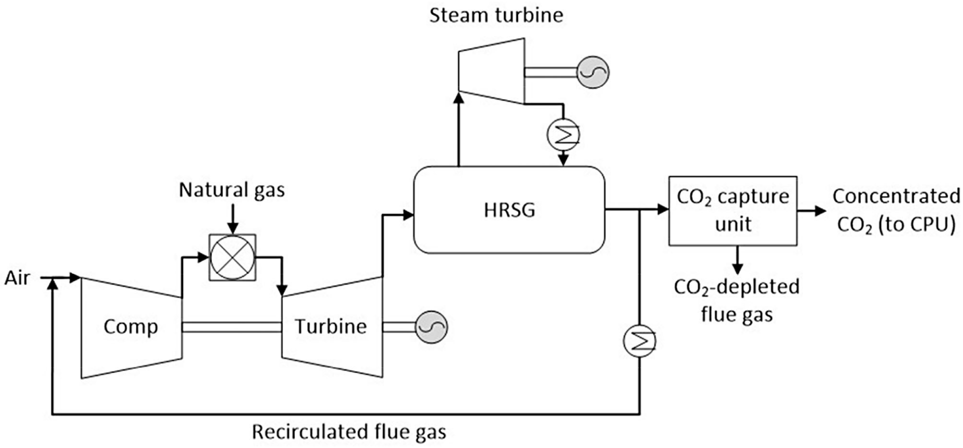

Figure 2. Schematic of NGCC plant with EGR and $CO_2$ capture plant.

combustor, at the expense of high CO and UHC levels. They also suggested that such emissions could be reduced during operation at higher pressures.[46] The increased CO concentrations are associated with insufficient $O_2$ for the oxidation reaction to $CO_2$, as well as reduced flame temperatures and speeds due to the higher specific heat capacity of the $CO_2$ concentrated in the oxidizer,[8,45–47] which may also lead to higher UHC concentrations due to incomplete combustion.[8,47,49,50] Reduced NOx concentrations have been observed in EGR combustion as a result of lower flame temperatures and reduced oxygen availability in the combustion air.[45,47] In this context, it is widely accepted in the literature that a minimum oxygen concentration of 16%vol. is required in the oxidizer for stable and complete combustion with current combustor designs,[8,16,46,51] thus ensuring flame stability and reduced emissions. This limits the maximum achievable EGR ratio to around 40%, leading to 6.5%vol. $CO_2$ in the flue gas fed to the capture system according to Li *et al.*[8] To increase beyond the 40% EGR ratio, new optimized combustor designs that allow appropriate combustion at an $O_2$ inlet concentration below 16%vol. and/or additional $O_2$ injection would be required.[8,46,47]

As indicated above, EGR improves the efficiency of the $CO_2$ capture process due to a higher $CO_2$ concentration in the flue gas and thus reduces energy demand compared to a conventional $CO_2$ capture plant. Net electrical efficiencies of ~50.6% have been reported for EGR capture systems.[39,47] This corresponds to an efficiency penalty of approximately 7 net percentage points with respect to a NGCC system without $CO_2$ capture, which is ~0.5 percentage points lower than that of NGCC plants integrated with conventional amine capture (without EGR).[39,47] Furthermore, the US Department of Energy (DOE) recently reported that $CO_2$ capture using amine absorption and 35% EGR ratio offers the lowest capture cost option for NGCC plants when compared to conventional amine capture plants without EGR.[39] In addition, modeling works,[8,15,22,48] laboratory[46] and pilot plant studies,[16,52] and patent applications[53] have shown the technical advancements and benefits of EGR. Demonstrating this technology at increasing scales of operation remains an obstacle. Thus, advancing the technological maturity of EGR, through demonstration pilot plant studies and adapted combustor designs will overcome the challenges and move gas-CCS with EGR forward.

## Selective exhaust gas recirculation

To limit some of the issues found with EGR, selective exhaust gas recirculation (S-EGR) has been proposed,[17] which uses a membrane system (or potentially another $CO_2$ separator) to concentrate $CO_2$ as illustrated in Figs 3 and 4. In this membrane, the combustion air acts as a sweep stream flowing counter-currently to the flue gas. As the membrane is selective for $CO_2$ over nitrogen and oxygen, $CO_2$ diffuses through the membrane into the combustion air sweep stream.[17] As depicted in Figs 3 and 4, the air stream, now rich in $CO_2$, flows to the compressor inlet, whereas the $CO_2$-depleted flue gas exits to the atmosphere. Since mainly $CO_2$ permeates the membrane, the combustion air is not diluted with nitrogen in S-EGR configurations, hence a higher $CO_2$ content is achieved in the flue gas than

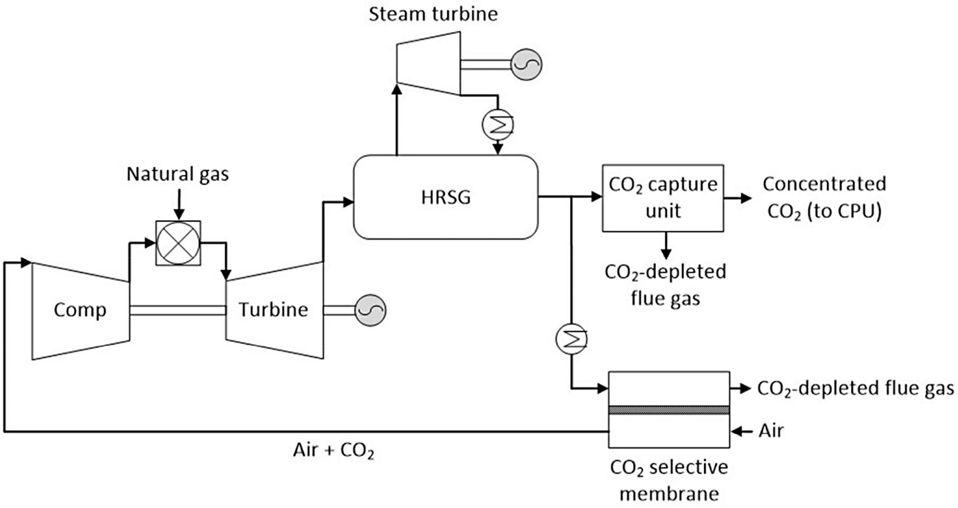

Figure 3. Schematic of NGCC plant with S-EGR parallel configuration and $CO_2$ capture plant.

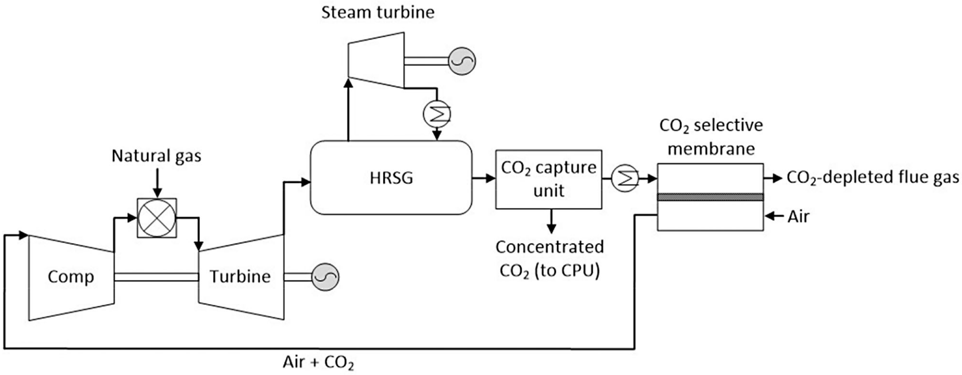

Figure 4. Schematic of NGCC plant with S-EGR series configuration and $CO_2$ capture plant.

with respect to EGR considered in the previous section. Merkel *et al.*[17] claim that the separation of $CO_2$ in the membrane from the flue gas towards the air stream is driven by the large partial pressure difference. This means that compressors or vacuums are not necessary (unlike in other membrane applications) and only blowers are required, reducing the energy input and capital costs.

Two hybrid S-EGR process configurations have been proposed, namely parallel and series operation.[17] Figure 3 illustrates the S-EGR parallel configuration, where the flue gas is separated after the HRSG into two streams that are fed to the selective membrane and the $CO_2$ capture unit, respectively. As a result, reduced flow rates of flue gas with higher $CO_2$ concentrations are treated in the capture plant, thereby reducing equipment size and process cost. This configuration requires a high $CO_2$ separation rate to be maintained in both the membrane and the $CO_2$ capture unit to achieve a high overall capture efficiency (~90%).

In the S-EGR series configuration, the entire flow of flue gas passes through the $CO_2$ capture unit and the membrane, as illustrated in Fig. 4. As can be seen, the flue gas is initially treated in the $CO_2$ capture plant, where only a fraction of $CO_2$ is captured. The exiting flue gas is then sent to the membrane system, where a fraction of the remaining $CO_2$ is transferred to the air stream and sent back to the inlet of the compressor. The advantage of this configuration is that the membrane performs as a $CO_2$ pre-purification system, and the individual $CO_2$ removal requirements for the capture unit to obtain an overall high capture efficiency similar to that of the parallel configuration described above are more relaxed.[17]

An initial energy analysis by Merkel *et al.*[17] illustrates S-EGR has the potential to reduce the minimum energy required to separate $CO_2$ from flue gas streams by up to 40%. These authors studied two S-EGR scenarios (corresponding to Figs 3 and 4), where $CO_2$ concentrations in the flue gas sent to the capture plant of 18.6%vol. and 13.7%vol. were achieved for the parallel and series configurations, respectively, while maintaining ~16%vol. $O_2$ at the inlet of the combustor,[17] as required for stable combustion.[8,16,46,51] Herraiz[24] also investigated these systems, calculating a $CO_2$ concentration in the flue gas entering the capture plant of 18.7%vol. for the parallel configuration, and between 6.7 and 12.9%vol. for the series system, whilst ensuring in both cases the $O_2$ levels at the inlet of the combustor are well above 16%vol.[24] However, the actual values of $CO_2$ content achieved in each configuration will vary depending on the $CO_2$ capture efficiency of the selective membrane and the capture unit (which determine the overall capture efficiency), and also on the S-EGR ratio allowed for the parallel configuration, defined as the ratio between the volume of gas treated in the selective membrane and the total volume of flue gas.

The potential advantages of S-EGR are promising, leading to a reduction in packing volume and reboiler duty of the capture plant.[24] However, the actual benefits will depend on a number of factors, notably, economic and technical issues. These include how S-EGR influences NGCC plant performance in terms of net power output and efficiency, effects on the turbomachinery, CAPEX, OPEX, upscale feasibility and commercial viability of this process. S-EGR can be technically feasible and the driver for this technology is the potential cost and energy penalty reductions associated with the $CO_2$ capture plant. The use of membranes in S-EGR capture systems requires high $CO_2$ permeability (~2000–2200 gpu) and moderate $CO_2/N_2$ selectivity of 20–50.[17] Membrane choice and flue gas conditions are also important factors when considering S-EGR systems, as these will influence cost and system performance. The short membrane lifetime (~ 3–5 years),[17,54] high initial and replacement membrane module costs and the impact of real flue gas conditions on membrane performance are challenges that need addressing to optimize S-EGR systems. Therefore, further research is required to overcome the challenges and advance S-EGR for gas-CCS applications (e.g. EPSRC EP/M001482/1 – SELECT project[55]).

## Humidified gas turbines

Adaptations of traditional gas turbine systems, such as gas turbine humidification through moisture inclusion in the cycle are being investigated to increase the electrical efficiency of gas-fired cycles, but also have benefits for CCS.[8,18,19,25] Such technologies change the working fluid from air to an air-$H_2O$ mix (by up to 20%) and are known as recuperative cycles since heat available in the process is recovered and reused to generate steam, which is employed to replace a fraction of the excess air.[18,19,26] 'Wet' or humidified turbines have the advantages of the high efficiencies of combined cycles and the low costs of open cycles. They have improved overall system performance compared to conventional gas turbines, through increased power and specific work outputs and improved thermal efficiencies. These systems also have lower NOx emissions (since $H_2O$ injection reduces peak flame temperatures) and higher $CO_2$ flue gas concentrations (in a smaller volume of flue gas, once the moisture is condensed out).[8,19,25,27] The latter reduces the energy penalty and costs for associated $CO_2$ capture.[8,25,27,28,56] Moreover, the part-load performance of humidified turbines is better than that of a combined cycle, and these systems can be used to compensate for the negative effect of increased ambient temperatures and/or reduced atmospheric pressures.[19,25] There are however drawbacks to such cycles, the primary ones being the increased costs, complexity and the consumption of large quantities of water, which often needs to be demineralized to avoid further issues, such as deposition and corrosion.[28]

Humidification can be achieved in two key ways, by the injection of water or steam.[18,19,25] Various techniques and configurations have been considered, although most research has been largely theoretical. These include the use of recuperative water-injected cycles (RWI), humid air turbines (HAT), top humid air turbines (TOP-HAT) and steam injected gas turbines (STIG).[18,19,25] RWI cycles show much more limited improvements in the efficiency and specific work compared to other humidified cycles, such as HAT,[57] whilst TOP-HAT configurations only achieve very small increases in the $CO_2$ concentration of the flue gas due to the low water injection rates associated with these systems.[19,58,59] Therefore, only HAT and STIG systems are discussed in detail below, since RWI and TOP-HAT configurations are not considered relevant for $CO_2$ capture purposes.

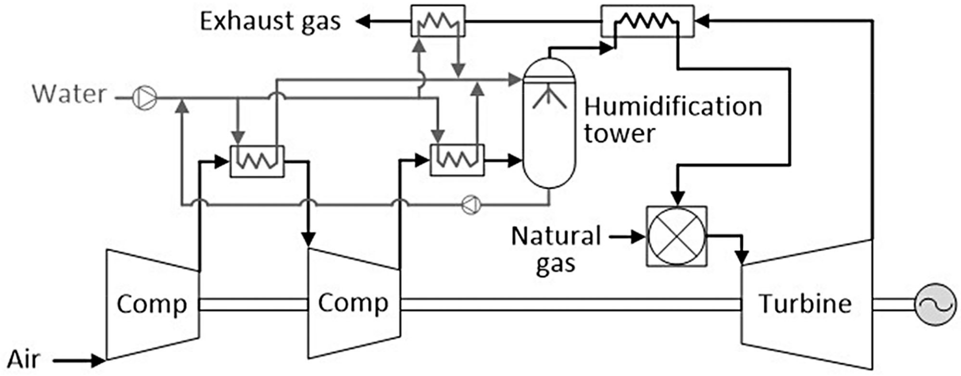

Figure 5. Schematic of a HAT system, outlining the water introduction in a humidification tower and its addition to the air at the compressor outlet.

## Humid air turbines

Humid air turbines, also known as evaporative gas turbines (EvGT), incorporate a saturator or humidification tower into the design.[18,19,27,60,61] As shown in Fig. 5, an intercooler and economizers are also included, to recuperate thermal energy from the compressor and the flue gases, respectively. This energy is used to heat and evaporate water in the humidification column, thereby saturating the air from the compressor outlet to give a single-phase mixture. The increased mass flow rate of the working fluid through the turbine results in a higher specific power output and greater thermal, electrical, and therefore total efficiencies than an equivalent dry cycle due to the additional turbine work.[18,19,27,58] HAT cycles evaporate water efficiently by using the low-temperature heat available in the cycle, thus reducing cycle irreversibilities when compared to other humidification options (e.g. STIG).[8,18] However, water consumption can be problematic, specifically adding significant cost, although intercooled cycles require a reduced amount of water but will still increase complexity.[58] The water added to the cycle will need to be condensed out and recycled, to reduce the rate of net water consumption and operational cost. This often needs treatment to ensure there is no build-up of contaminants in the recycled stream. Also, at high water-fuel ratios, increases in emissions relating to incomplete combustion are found, specifically CO and UHC.[28] Another limitation is that suitable turbomachinery for HAT-type systems still needs to be developed, as they need to cope with a flow mismatch between the compressor and the turbine as a result of humidification.[18,19] Therefore, HAT systems have not yet achieved commercial scale utilization.

Experimental work has primarily been highly focused on examining ways in which the performance of saturators and humidification towers can be assessed and improved[62–66] rather than on the performance of the turbine or capture system. Technical aspects of the whole cycle (such as in Wei and Zang[56]), or how improvements can be made to aid carbon capture (like in Li *et al.*[8]) have received significantly less attention.

For HAT systems, the highest cycle efficiencies and the largest specific work outputs are achieved when operating with both high humidity ratios and high compressor pressure ratios.[56] Models of HAT systems have quantified the improvements in performance in terms of the thermal efficiency and power output compared to simple and combined cycles, as well as other means of improving the performance or increasing the $CO_2$ concentration. High electrical efficiencies are achievable at a wider range of pressure ratios, much more than for a simple cycle. Typical efficiencies of simple cycles are 25–40%, whereas for HAT designs the efficiency often exceeds 50%, with some reporting values greater than 55%.[67,68] The performance of HAT cycles with and without $CO_2$ capture has been assessed against combined cycles by Li *et al.*[69] They found that the optimum water/air ratio (defined as the ratio between the mass flow rate of evaporated water and that of air) for HAT systems without $CO_2$ capture was 0.14, which corresponds to an electrical efficiency of 52.1%. A HAT configuration with $CO_2$ capture was also evaluated, using aqueous monoethanolamine (MEA) at 30%wt. as the solvent in the scrubbing system. In this case, the highest electrical efficiency (41.6%) was obtained at a water/air ratio ~0.12. Nevertheless, these HAT cycle efficiencies were found to be lower than those of conventional combined

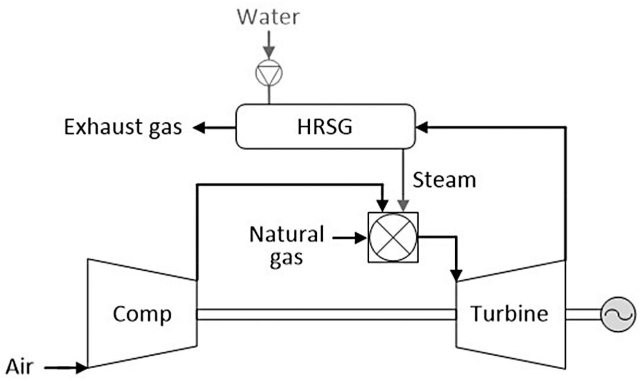

Figure 6. Schematic of a STIG system, where steam is introduced directly into the combustion chamber from a HRSG.

cycles, 47.9% and 56.7% with and without $CO_2$ capture, respectively.[8] The operating costs of HAT systems can be high compared to NGCCs,[70] although they may be competitive for small-scale applications, where steam cycles have reduced efficiencies and higher costs.[18] Moreover, only limited $CO_2$ increases can be achieved with this technology (up to ~5%vol.), and the higher $H_2O$ concentrations in the flue gas may dilute the amine solution in the absorber and increase the energy consumption of the $CO_2$ capture process.[8] As a result, combing HAT with CCS in large-scale systems is often not considered for economic reasons.[70]

## Steam-injected gas turbines

Steam-injected gas turbines are where steam is used instead of water and is injected directly into the combustion chamber as a separate stream, rather than being added with the combustion air/working fluid.[18,19,25,58,60,71] As seen in Fig. 6, water evaporation occurs in the HRSG, using the heat supplied by the hot turbine outlet gases. Stable operation of the gas turbine system can be achieved with the injection of steam into the combustor and the efficiency can be improved in this way when compared to the same set-up without an injection of steam. As in other humidified designs, this is a result of the increase in the mass flow rate through the turbine, whereas the compressor power remains unchanged.[18,19,25] Moreover, the CAPEX of STIG systems may be lower than that of combined cycles (especially at scales <50 MW), since often no steam turbine and associated equipment are used in these cycles.[18] However, steam injected gas turbines also have limitations, including corrosion issues that require the use of high-quality water.[18,19] As with the other concepts, water consumption can be problematical, often more so for these designs, which can have water utilization rates of up to three times greater than HAT systems, since process losses are considerable.[26,61] Additional effects are related to the flow mismatch between the compressor and the turbine because of the steam injection. This requires the use of higher pressure ratios in the compressor if the same turbine geometry is used, and limits the amount of steam to be added.[18,19] Further effects of the different working fluid composition and thermodynamic properties in the turbine performance also appear.[19]

Steam injection rates up to 19% of the air mass flow to the compressor can be achieved in STIG systems.[19] Improvements to the efficiency are significant for a STIG compared to a simple gas turbine cycle (by more than 10% points), however, they have lower efficiencies than combined cycles.[19,72] Developments and adaptations have been made to the basic STIG technology, including the use of intercooled STIGs, combined STIG cycles and so-called FAST cycles, to increase the work done by the turbine.[58] STIG cycles typically have efficiencies of 38–48%, which can be improved further if formed into a STIG-based combined cycle, where values in excess of 60% have been reported.[73,74]

STIG technology is already available at commercial scale.[18,19] However, these systems use turbines initially designed for dry cycles and therefore are limited in the amount of steam that can be injected. As a result, lower efficiencies (typically in the range of 37–41%[18,19]) than those reported in the theoretical studies are obtained, although they can be increased up to 50% by using a further advanced configuration that includes intercooled compression (such as the GE LMS100 – 60 Hz).[19] Nevertheless, efficiency values are lower than those of combined cycles, and STIG systems are more viable for small-scale applications (a few MWs), where combined cycles are not an option due to technical and cost issues.[18,19] This limits the interest of STIG configurations for $CO_2$ capture on a commercial scale.

## $CO_2$ capture systems

Significant effort has been devoted to analyzing post-combustion capture technologies for power plants using coal, whilst there is a more limited number of $CO_2$ capture studies focused specifically on gas-fired systems. However, gas-CCS is currently receiving increased attention,[4] with amine scrubbing being the subject of numerous studies for post-combustion $CO_2$ removal.[4,23] The use of emerging $CO_2$ capture technologies or additional solvents for gas-CCS applications is also being actively investigated as an alternative to amine capture systems. This is the case of the chilled ammonia process, which is being tested in a pilot plant located in Mongstad (Norway). This plant can a treat either refinery off-gas or a flue gas from a gas turbine combined heat and power unit ($CO_2$ concentration between 4 and 13%vol.),[75] although only limited results/studies are publicly available.[75,76] Configurations using calcium looping technology for NGCCs have been also recently analyzed,[77–79] even in combination with the exhaust gas recirculation strategy discussed above.[80] The use of membranes has also been proposed, using different configurations, multi-stage membrane layouts and/or EGR and S-EGR to enhance the driving force for the $CO_2$ separation.[17,81–85] More complex options have been also explored, such as the use of molten carbonate fuel cells in combination with gas membranes[86] or with $CO_2$ cryogenic separation.[87]

Amongst all the alternatives mentioned above, $CO_2$ capture using amines is currently regarded as the most advanced post-combustion technology, with two plants already operating at commercial scale (for coal applications). Therefore, this perspective focuses on this technology for primarily discussing post-combustion $CO_2$ capture and the main barriers that should be overcome for its wide deployment as a gas-CCS technology.

## Amine capture plant systems

Post-combustion carbon capture using amine-based solvent scrubbing is the most mature and understood process for recovering $CO_2$ and is a leading candidate for gas-CCS applications. A schematic of the process is shown in Fig. 7; as seen, the process uses a liquid flowing counter-currently to the flue gases to absorb $CO_2$ in a packed tower, namely the absorber. For this purpose, the absorption tower (as well as the stripping tower described below) normally employs random packing due to its ease of installation and lower costs, although nowadays structured packings are getting more attention due to their lower pressure drop and better gas-liquid contact. The solvent enters the absorber from the top while the flue gases enter from the bottom, both at ∼40°C, and an exothermic reaction takes place between the solvent and $CO_2$ along the reactor.[9] As a result, the $CO_2$-depleted gas stream is released into the atmosphere after a subsequent washing stage and the $CO_2$-rich solvent exits the bottom of the absorber. The rich solvent is then pumped into the top of the stripping tower, where it is heated up by the upcoming stream of $CO_2$ and steam generated in the reboiler, after passing through a previous pre-heating stage. The solvent releases a fraction of the $CO_2$ in the stripping tower before it passes through the reboiler, where the remaining $CO_2$ is removed at a temperature in the range of ∼120–130°C and usually at an elevated pressure (∼1.2–1.8 bar). To attain such temperatures, the reboiler is usually heated up using low-pressure steam. Many different amine-based solvents are available for $CO_2$ capture; however, aqueous monoethanolamine is the most widely used because it is the most well-known.

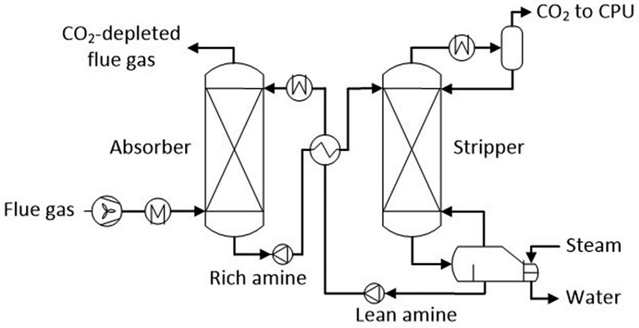

Figure 7. Basic schematic of the amine PCC process.

Despite the proven performance of these systems, the main limitation of the amine scrubbing process of Fig. 7 is that it is very energy intensive. It requires around 4 MJ/kg $CO_2$ captured when using MEA for $CO_2$ capture from a flue gas generated in gas-fired power plants.[8] This involves a significant energy penalty on the power plant, which results in a decrease in its net efficiency by up to 11 net percentage points.[88] This adds up to the large flows of flue gas with low $CO_2$ concentrations that need to be treated in the amine capture plant, which increases the capital and operational costs of $CO_2$ capture. Therefore, significant effort is being devoted to enhancing the performance and reduce the energy requirements and cost implications of amine capture plants to make the post-combustion capture process economical.

Pilot and demonstration-scale studies are being carried out widely. However, commercial-scale facilities are very rare and focused on coal combustion applications. According to the Global CCS Institute database,[89] there are currently only two large-scale power generation CCS projects, namely Boundary Dam and Petra Nova. As indicated in the *Introduction*, Boundary Dam (Canada) entered operation in 2014, becoming the first amine $CO_2$ capture plant at commercial scale in the world. It belongs to Sask Power and is capable of capturing 1 Mt $CO_2$/year from a 139 MW lignite-fired power plant with 90% capture efficiency using the Shell Cansolv process.[5] Moreover, the Petra Nova project became operational recently in the USA and is the world's largest operational commercial-scale post-combustion CCS project so far with a capacity of 1.4 Mt $CO_2$ captured/year.[6] This capture plant uses an amine-based solvent (KS-1) developed by Mitsubishi Heavy Industries and is capable of capturing $CO_2$ from a flue gas slip stream corresponding to 240 MW of coal combustion with more than 90% capture efficiency.[6] In addition to these commercial-scale plants, there are also several pilot and demonstration projects worldwide. Similar to the commercial-scale plants mentioned, most of the currently operational pilot plants using amine solvents for $CO_2$ capture treat flue gases generated from coal combustion, although in many cases modifications are made to the process to change the flue gas characteristics to reflect the compositions and specific features from other combustion processes, such as natural gas combustion. There are only a limited number of pilot plants that treat flue gases directly derived from gas combustion processes. This is the case of the amine pilot plant built at the $CO_2$ Technology Centre Mongstad in Norway, which can capture 20 kt $CO_2$/year from a natural gas-fired Combined Heat and Power (CHP) power plant.[90] Sulzer CCS pilot plant in Switzerland has the capability of treating up to 150 kg/h of flue gases generated from a commercial gas fired burner designed for heating homes. The burner can deliver 3.8%vol. $CO_2$ concentration in the flue gas, typical of NGCC power plants.[91] A 380 kW propane burner is used as the flue gas source at the SINTEF pilot plant, which has 50 kg/h of $CO_2$ capture capacity and is located at Tiller, Norway.[92,93] The burner produces a flue gas with a $CO_2$ concentration of 9%vol., which can be diluted to represent gas turbine flue gas conditions or concentrated with $CO_2$ before being fed into the absorber.[92] Moreover, the UK Carbon Capture and Storage Research Centre (UKCCSRC) Pilot-scale Advanced $CO_2$ Capture Technologies (PACT) facilities encompasses a 1 t $CO_2$/day capture plant capable of treating flue gas from a 330$kW_{th}$ micro gas turbine (as well as from a 250$kW_{th}$ coal/biomass/co-firing furnace or from a custom made gas from a gas mixing facility). The composition of the flue gas leaving the micro gas turbine which is fed into the capture plant ranges from 1.5 to 6.3%vol. $CO_2$. This is as a result of $CO_2$ injection into the micro gas turbine compressor inlet, to simulate different gas compositions typical of EGR/S-EGR processes.[52] The $CO_2$ concentration of the flue gas going to the capture plant can also be varied by directly injecting $CO_2$ into the slip stream.[16]

The results obtained in the commercial and pilot plants mentioned above and in further process simulation studies indicate that there are opportunities for significant process improvements, which have the potential to reduce capital and operational costs. These include process optimization, development of novel/gas-specific solvents and improvements in the operational flexibility and overall economics, which are considered in detail hereunder.

## Process optimization

A number of different techniques are currently being investigated to improve the performance of the PCC process, including absorber performance enhancement, heat integration and the use of heat pumps.[94] Employing a rotating packed bed column in the absorber, which is a rapidly emerging absorption enhancement option, has been proposed as an alternative to the use of conventional packed columns. These towers make the fluids spin at high speeds using centrifugal forces instead of gravitational forces, making the solvent and gas flow outwards and inwards, respectively. The rotating towers have shown to favor gas-liquid contact, thus improving the reaction rate.[95,96] The towers can be operated in multiples either themselves or in combination with conventional packed towers and in different configurations, namely series and parallel. Yu *et al.*[97] studied this system for a flue gas with 10%vol. $CO_2$, and indicated that a configuration with two rotating packed beds in series gives the highest performance and can decrease regeneration energy by 9.5% due to the increase in the solvent rich loading. Other absorber enhancement configurations include the use of an intercooled absorber or a rich solvent recycle, which can lead up to 20% or 4–5% decrease in the reboiler energy demand, respectively.[94] Further alternatives are the use of an interheated absorber, a split-flow arrangement, a double loop absorber or flue gas compression and expansion.[94]

Heat integration options have been also proposed to reduce the reboiler duty. This is the case of rich solvent splitting, preheating or flashing, or advance flash stripper configurations amongst others, which can achieve energy savings in the amine capture plant of up to 45%. According to Pan *et al.*,[98] HRSG heat transfer intensification can increase heat recovery up to 7% with minimal plant modifications. Additional heat integration options between the amine PCC system and the power plant can be also beneficial, such as the use of low-pressure steam instead of saturated steam, which can reduce the reboiler area by up to 48%.[98] Advanced flash stripping, where hot solvent leaving the reboiler is flashed in a flash tank and the vapors released are compressed before entering the stripper, have shown to improve the heat duty by 16% compared to a simple stripper.[99] A combination of an advanced flash stripper and rich solvent bypass (combination of hot and cold bypass) decreased the heat duty by over 25% compared to a two-stage flash stripper configuration.[100]

## Novel solvents

Another parameter which contributes to operational costs is the solvent used for capturing $CO_2$. As already indicated, MEA is the most widely used solvent, but it has a number of drawbacks such as high reboiler duty, low absorption capacity, poor thermal stability and high corrosivity.[101] These issues lead to high energy penalties and capture plant OPEX. Values of reboiler duty using MEA vary considerably depending upon the estimation methodologies and optimization strategies employed, but are typically between 3.5 and 4 MJ/kg $CO_2$ for optimized systems.[102] Thermal degradation of MEA is low at temperatures below 110°C but increases with temperature and pressure. At 135°C, the degradation rate could be as high as 6% per week.[103] The presence of oxygen in the flue gas also causes issues, for example, oxidative degradation of MEA, leading to higher OPEX.[104]

New alternative solvents, such as cyclic amines, hindered amines, ether amines, amino acids, phase change solvents, ionic liquids, either single or mixtures are being investigated to enhance the capture process performance.[105–107] The mixtures of solvents take the advantage of fast kinetics of primary and secondary amines as well as high absorption capacity and low regeneration energy of tertiary and sterically hindered amines.[108]

Some of the new solvents developed have shown promising results in terms of kinetics, solubility, and mass transfer, as well as regeneration energy over the conventional MEA solvent.[109–111] ABB Lummus, MHI KS-1 solvent, Fluor's Econamine FG PlusSM Technology, Cansolv amine process and Praxair MEA-MDEA process are commercialized and claim, over other benefits, to have reduced regeneration energy requirements over conventional MEA processes.[10,112] The Cansolv process has claimed to be using 40% less energy for regeneration as compared to Econamine process subject to clarification[10] while Econamine FG Plus and Praxair require ~3.2 MJ/kg $CO_2$[113] and 3.0 MJ/kg $CO_2$,[10] respectively. Econamine FG Plus process has been reported to be specifically designed for gas turbine flue gas streams.[112] A solvent (CESAR1) that uses 20% less energy for regeneration (3.2 MJ/kg $CO_2$) as compared to MEA has been developed.[114] Zhang *et al.*[115] investigated solvent properties in order to find out the optimum solvent for low $CO_2$, high $O_2$ concentration flue gases typical of gas-fired power plants. By studying vapor liquid equilibrium data of different potential advanced solvents including secondary, tertiary and hindered amines and their blends, they observed that cyclic $CO_2$ capacity of 2-dimethylaminoethanol (DMAE) and 2-Amino-2-methyl-1-propanol (AMP) based solvents is twice that of MEA. Moreover, it was found that dissolution of $CO_2$ into the aqueous solvent solutions studied increases if the primary amine is partially replaced by piperazine (PZ).[115]

Despite all the efforts carried out, key scientific challenges remain. Next-generation solvents should be specially formulated for gas-CCS applications taking into account the particular characteristics of these systems, exhibiting lower energy requirement and higher chemical and thermal robustness to withstand other flue gas constituents and impurities such as $O_2$, CO and NOx over longer term.[116]

## Flexibility

Gas-fired power plants are normally used as backup utilities and operate at variable loads.[4] Therefore, a major challenge in the design of PCC amine plants integrated with gas-fired plants is that they should be flexible to follow the load changes in the power plant. The behavior of amine PCC plants and their economic and environmental impact during flexible operation is not well understood at the moment, although it has recently attracted a great deal of attention.[11,117–122] Optimization of the capture plant during dynamic operation is a crucial element to reduce overall operational costs and ensure the stable and efficient performance of the capture plant at all times. Different techniques have been proposed to increase the power output from power plants coupled with amine PCC systems at peak demand periods. These include turning down or turning off the capture plant for a certain period to generate extra power, storage of the rich solvent generated for subsequent regeneration during low demand periods and storage of $CO_2$. This is to supply a constant $CO_2$ flow to the transport lines and storage sites, which can avoid issues relating to intermittent $CO_2$ flows.[11] From a peak load point of view, NGCC plants designed with an integrated capture plant could perform better than those designed without integrated capture, as the capture plant can be turned down/off at the same time as increasing the load of the power plant.[11] This will give higher margin between peak load and base load conditions, at the cost of increased $CO_2$ emissions. In those cases, it may be required to install an auxiliary boiler to provide steam to the stripper during this period[117] or to capture $CO_2$ at a higher rate during normal operation to compensate for higher emissions at peak loads and meet emissions regulations.[11]

Advanced integration options between the power plant and the PCC amine system have also been considered for load-following operations, including flexible steam extraction from the power plant using a throttled low-pressure steam turbine or with a floating intermediate/low-pressure crossover pressure.[122] Start-up operations in NGCCs can be challenging for associated amine PCC plants. Gas turbines start up quickly compared to HRSGs and steam turbines. During this period, the gas turbine will produce flue gas, which can be initially absorbed by the solvent in the capture plant, but steam will not be available to strip the $CO_2$ from the solvent.[11] An option is to emit this flue gas without capturing $CO_2$, which can be minimized by appropriate design changes to the capture plant.[117] Other options involve installing an auxiliary boiler to provide steam to the stripper during this period[117] or to design the capture plant with storage capacity for both the rich and lean solvents.[11] In this case, it would be possible to operate the capture plant by feeding the absorber with a lean solvent from the lean storage tank and store the rich solvent leaving the absorber in a rich storage tank. During this period, the stripper will be idle. The rich solvent from the rich storage tank can be regenerated at a later time when power demand is lower.[118] However, this option offers a marginal benefit and comes with an additional cost of huge solvent inventory and associated regulatory liability.[119]

Further work is required to develop the flexibility options described herein or find potential new alternatives. In addition to this, techniques should be developed for real-time solvent loading measurement[120] to control the PCC plant in an optimized way during transient operation. For this purpose, model predictive control has been proposed as a tool to control the PCC plant by optimization against disturbances caused by load following mode of operation.[121]

### Overall economics

Economic performance of amine PCC plants is highly dependent upon operational parameters such as the $CO_2$ loading, liquid-gas ratio, amine concentration in the solvent and stripper operating pressure.[123] A parameter often used to compare the cost of electricity in different scenarios is the levelized cost of electricity (LCOE). According to US Energy Information Administration,[124] for advanced NGCC plants entering service in 2022, estimated averaged LCOE will be around 48% higher for the plant equipped with $CO_2$ capture ($84.8/MWh) than those without capture ($57.2/MWh), although these figures may vary depending on the possibility of increased burden on carbon prices in the future.

## Oxy-fired gas turbines

Oxy-combustion is an alternative option for $CO_2$ capture from natural gas. Unlike the configurations described above, oxy-combustion is a CCS technology itself, so there is no need for any additional $CO_2$ capture plant downstream. Instead, an almost pure $CO_2$ stream suitable for final purification, compression and storage purposes is delivered after combustion and the subsequent expansion and heat recovery stages. Consequently, one of the most important benefits of oxy-fired cycles is that $CO_2$ emission reductions can reach almost 100%. In oxy-combustion systems fuel is burned in an environment free of nitrogen, using an $O_2/CO_2/H_2O$ mixture instead of air. An air separation unit (ASU) is required to strip the $O_2$ from the air to be provided for combustion. The ASU is very energy intensive and also adds considerable capital and

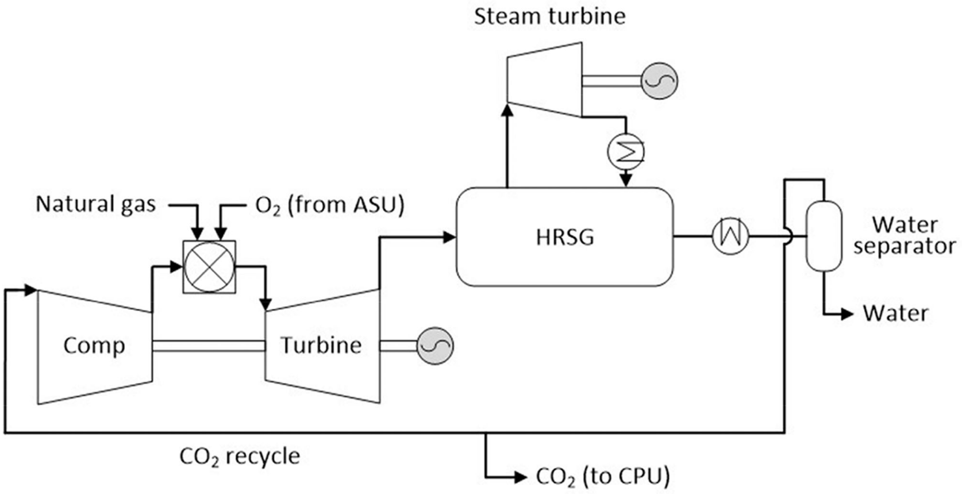

Figure 8. Schematic of the SCOC-CC configuration.

operating costs.[15,30] Therefore, oxygen requirements are usually kept to a minimum by performing oxy-combustion at close to stoichiometric conditions. Since combustion in an oxygen-rich environment occurs at excessively high temperatures, recirculating a high proportion of the flue gases provides a diluent for the $O_2$ and lowers the temperatures to manageable levels. The recycled stream will be predominantly $CO_2$ and/or $H_2O$, i.e., for $CO_2$-based and water-based oxy-combustion cycles, respectively.[29,30] As will be discussed in detail later, the former includes semi-closed oxy-combustion combined cycles and high-pressure $CO_2$ supercritical cycles, whereas water-based cycles comprise the CES and Graz cycles.[29,30,125] Other alternative configurations integrate oxygen production in the cycle by using high-temperature membranes (i.e., ZEITMOP and AZEP cycles). However, these are not considered in this work because of their relatively low technology readiness level.[29] Chemical looping combustion concepts are also being studied to avoid the need for an ASU and, therefore, reduce the energy penalty in gas-fired systems. However, substantial progress is still needed for these systems to operate at the high temperatures and pressures required to achieve competitive efficiencies when compared to NGCC power plants[126–128] and therefore, these are not being examined in detail herein.

## Semi-closed oxy-combustion combined cycles

Semi-closed oxy-combustion combined cycle (SCOC-CC) systems use $CO_2$ as the working fluid, as depicted in Fig. 8. Their configuration resembles that of conventional NGCC power plants but using oxygen instead of air as the oxidizer stream in the combustor.[15,29,30] The flue gas, mainly composed of $CO_2$ and steam, expands throughout the gas turbine, and then passes through the HRSG unit, where heat is transferred to the steam cycle to generate additional power in the steam turbine. After that, the flue gases are further cooled to condense and separate water. This stream is then split into two, with a fraction being recirculated to the inlet of the compressor and another fraction being sent to the compression and purification unit (CPU) for subsequent $CO_2$ storage/use.[15,29,30]

As already indicated, the configuration shown in Fig. 8 can supply a stream of high-purity $CO_2$ without any further $CO_2$ separation process. However, the composition and properties of the working fluid are very different when compared to conventional air-fired NGCC cycles. As a result, the pressure ratio should be optimized, leading to values around 30–40 for turbine inlet temperatures around 1300–1400°C.[29,30] Redesigning components will be required, especially in the case of the combustor (operating at a high pressure in an $O_2/CO_2/H_2O$ atmosphere), the compressor and

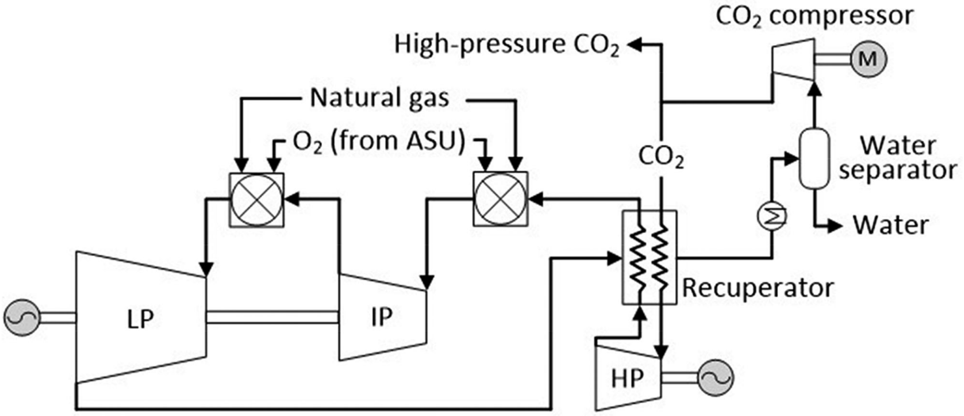

Figure 9. Schematic of the MATIANT cycle.

gas turbine, although the HRSG components can often remain the same since the turbine outlet temperatures are comparable here.[29,30] The reported overall efficiency of such systems is between 45 and 49%.[29,30] Since retrofitting is not possible with this configuration, new construction would be required at high CAPEX; although most components required are generally already available on commercial scales, blade designs may need to change to reflect the alterations in working fluid. Furthermore, although the efficiencies achieved can be high, other advanced cycles considered in Section 3 below offer greater efficiencies.[29]

## High-pressure $CO_2$ supercritical gas turbines

In addition to the systems described above, there are also oxy-fuel cycles which make use of $CO_2$ at supercritical conditions in gas turbines without a bottoming steam cycle (critical point of $CO_2$: 31°C, 74 bar).[29,30] This is the case of the MATIANT cycle and the Allam cycle (also named NET power cycle), which are summarized in this section. The MATIANT cycle has been proposed by Mathieu and Iantovski[31] and is illustrated in Fig. 9. As indicated in this figure, the $CO_2$ stream first undergoes multi-stage intercooled compression up to 300 bar. A fraction of this fluid is taken for $CO_2$ storage purposes and/or enhanced oil recovery (EOR), whereas the remaining $CO_2$ passes through the recuperator, where it is heated up to around 600°C.[31] The supercritical $CO_2$ is then expanded through a high-pressure turbine to 40 bar, and is reheated in the recuperator to around 700°C before entering the first combustor.[31] This combustor is fed with natural gas, which is burnt under oxy-fired conditions. The obtained $CO_2$ at high temperature (~1300°C) is expanded in an intermediate pressure gas turbine to around 9 bar and is heated up again (~1300°C) in a second oxy-fired combustor. The resulting fluid is expanded to atmospheric pressure and is used afterwards as the hot fluid in the recuperator. Before recirculating the $CO_2$ back to the inlet of the initial compression system, a final cooling stage is carried out, where water is condensed and separated.[31] The MATIANT cycle described here is similar to the COOPERATE cycle proposed by Yantovski *et al.*[129] The difference is that $CO_2$ entering the first oxy-fired combustor in the COOPERATE cycle is not reheated after the expansion in the high-pressure turbine.[29] Cycle efficiency values of between 35.4 and 49.3% have been reported for the MATIANT cycle, depending on the isentropic efficiency of the $CO_2$ compressors (varied between 65 and 90%) and the pressure achieved after the expansion in the high-pressure turbine (varied in the 40–100 bar range); these were found to be the most influential parameters.[31,130] Further variants of the MATIANT cycle, i.e., E-MATIANT[131] and CC-MATIANT,[132] have also been proposed in order to increase the efficiency of the process.[29]

The use of supercritical $CO_2$ as the working fluid for CCS purposes is also the basis of the Allam cycle – Fig. 10 illustrates this in its gas variant. This cycle has been recently proposed by Allam *et al.*[32] and uses only one high-pressure $CO_2$ turbine. In this case, the $CO_2$ is first compressed up to 200–400 bar in an intercooled multi-stage compression system. Then, it is heated up to a temperature of 700–750°C in the recuperator prior to entering the combustor. This heat is supplied by the fluid exiting the turbine and a fraction of the low-temperature heat (100–400°C) generated in the air compressors of the ASU ($Q_{ASU}$ in Fig. 10).[133] The

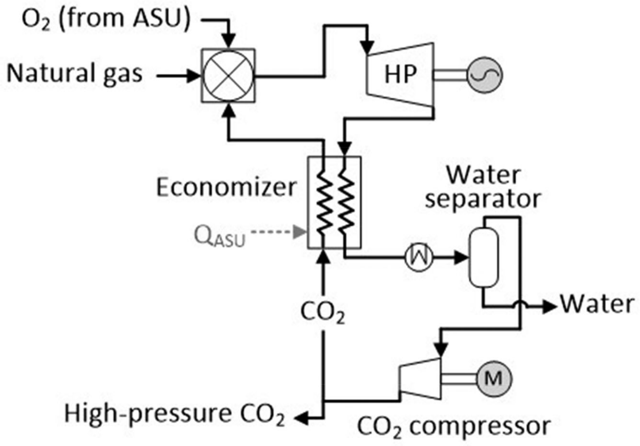

Figure 10. Schematic of the Allam cycle.

combustor operates under oxy-firing conditions, using natural gas as the fuel and oxygen produced in an ASU, leading to a combustion gas temperature of around 1100–1200°C.[133] This high-temperature, high-pressure stream is then fed to the turbine, where it expands below the critical point of $CO_2$ (e.g. 30 bar – pressure ratio of between 6 and 12).[134] This stream supplies heat to the supercritical $CO_2$ in the recuperator and is then further cooled down. After water separation, the $CO_2$ is compressed again. A fraction of this stream is sent back to the recuperator to initiate the cycle, whereas part of the $CO_2$ is sent for storage and/or other uses (e.g. EOR). High cycle efficiencies in the range of 55.1% and 58.8% have been calculated for this cycle.[29,134]

The supercritical $CO_2$ cycles described above have several potential advantages. These include high cycle efficiencies with almost no emissions of $CO_2$ to the atmosphere, without coupling to a $CO_2$ capture plant. Zero (or low) NOx emissions are generated due to the replacement of air by an $O_2/CO_2$ mixture as the oxidant in the combustor.[133] Also, Allam *et al.*[133] claim that smaller components will be required due to the use of high pressures in the cycle, thereby leading to a smaller footprint. They estimate the CAPEX of the Allam cycle for gas applications may be \$800–1000/kW, with ⅓ of the footprint of an NGCC power plant with similar power output.[133] However, supercritical $CO_2$ cycles are still at an early stage of development. Addressing important technology challenges, mainly derived from the high pressures of operation, the need for large duty recuperators and the use of $CO_2$ as working fluid in the cycle is required.[135] For the MATIANT cycle, a number of components have been identified as critical.[29] This is the case of the medium- and low-pressure $CO_2$ turbines, which require a new design because of the different properties of the working fluid. The recuperator is also expected to need large surfaces and expensive materials capable of withstanding high pressures and temperatures of operation.[29] $CO_2$ compression should be also carefully designed to avoid $CO_2$ condensation before the final compression stage and minimize energy consumption.[29]

Similarly, the development of the Allam cycle also presents several technological challenges.[29,30,133] The $CO_2$ turbine operates at conditions that combine very high pressure and temperature. This is far from the capabilities of current commercial components so that a new design that combines the features of supercritical steam turbines and high-temperature gas turbines would be required.[29,30,133] Also, stable and highly efficient combustion should be achieved at around 300 bar and 1150°C, using a mixture of $O_2/CO_2$ as the oxidizer. No combustor operational experience is available at commercial scale under these conditions, although R&D activities are currently ongoing. Recently, a reduced-scale combustor was tested by Toshiba, achieving successful ignition and initial combustion at ~300 bar and 1400°C for 80 s.[136] Material R&D is also essential for the development of the turbine and combustor equipment.[133] The recuperator is another critical component because of the high $CO_2$ flow and high pressures and temperatures of operation, which require large heat transfer areas and expensive materials.[29,133] Hence, it will have an important effect on the costs of the system of Fig. 10.[29] A 50 $MW_{th}$ demonstration facility is being built by NET Power in Texas, to advance the development of the Allam cycle, reduce associated uncertainties and validate the technology.[137]

## CES cycle

The CES cycle (an advanced humidified oxy-cycle developed by Clean Energy Systems) uses steam (up to 90%vol.) and $CO_2$ (~10%vol.) as the working fluid for nearly zero emissions power generation.[34,138] This essentially involves replacing traditional steam boilers and the flue gas clean-up sections with a 'gas generator', where natural gas is burnt with oxygen using liquid water to control the temperature in this high-pressure combustor (around 50–100 bar),[29,30,34,139] as shown in Fig. 11. Water evaporates in the combustor and the resulting working fluid (mainly $H_2O$) is expanded in a high-pressure steam turbine (pressure ratio ~5).[139]

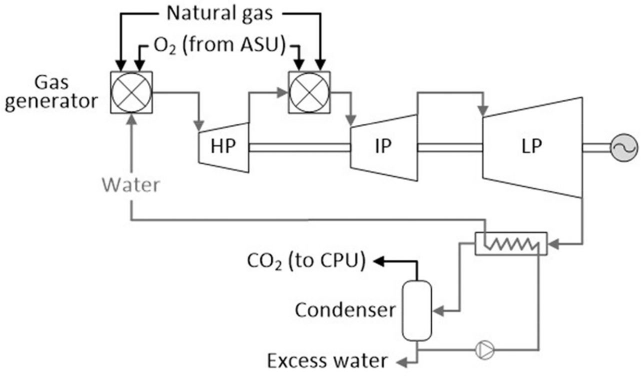

Figure 11. Schematic of the CES cycle.

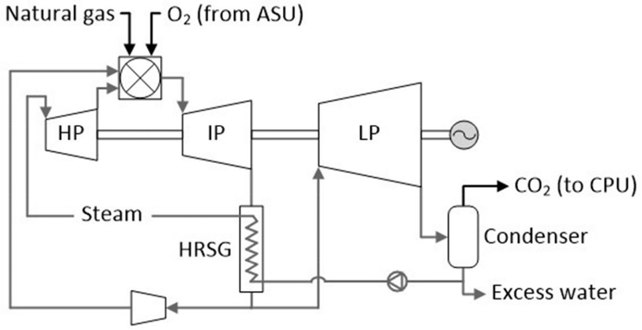

Figure 12. Schematic of the S-Graz cycle.

Subsequently, it is reheated in a second oxy-fired combustor and expanded in the intermediate- and low-pressure turbines. The water is then condensed out (leaving the $CO_2$ to go to sequestration) and recycled to the gas generator after preheating with the gas that exits the low-pressure turbine.[29,30,138]

The efficiency of the CES cycle is in the range of 43–50% and depends on many variables, such as the inlet temperature of the high-pressure turbine and the condenser pressure.[29,30] The intermediate-pressure turbine inlet temperature is especially influential and substantially increases the CES cycle performance when 1150–1260°C or higher.[139] A major technical challenge is, therefore, the development of the intermediate-pressure turbine at increasing temperatures of operation since its working conditions are similar to those of gas turbines despite using a steam-concentrated fluid.[139,140] A 20 $MW_{th}$ pilot test facility has assessed the operation of the high-pressure, high-temperature gas generator, at temperatures $>1600°C$ and pressures in excess of 100 bar,[34] and it is reported that the CAPEX can be half that of a combined cycle turbine.[138] It has more recently been reported that the CES cycle produces favorable results in terms of technology and environment; however, it is still under development to demonstrate the technology.[125]

## Graz cycle

The Graz cycle was initially proposed by Jericha[141] and was then further developed by Sanz *et al.*[33] These authors proposed a more advanced configuration named the S-Graz cycle, which uses high steam contents and achieves higher efficiencies. The S-Graz cycle configuration is represented in Fig. 12. It makes use of steam to control the temperature in the combustor, which operates at around 40 bar under oxy-fired conditions. The generated flue gas, mainly composed of steam and $CO_2$, exits the combustor at $\sim$1400°C and expands in a gas turbine to atmospheric pressure. Then, it passes through an HRSG unit where it cools down to around 180°C before being split into two streams, both with high steam content. One of these streams is compressed and recycled back to the combustor to moderate the temperature in this unit. The other is expanded in a low-pressure gas turbine to vacuum conditions and then passes through a condenser. The separated $CO_2$ is then compressed and taken for storage, whereas the condensed water is pumped and passed through the HRSG to generate high-pressure steam ($\sim$180 bar, 550°C). The steam is then expanded in a high-pressure steam turbine and is used as the second recycle stream to the combustor for temperature control purposes. A variation of this cycle that avoids steam condensing at vacuum conditions has also been proposed, namely the modified S-Graz cycle.[142]

Calculated efficiencies of the different Graz cycle configurations between 49 and 54% have been reported.[29,30] In terms of efficiency, the Graz cycle is the second most promising oxy-combustion option, after the Allam cycle described above.[29] However, some limitations should be addressed for its development. These are related to the turbine placed after the combustor, which operates at much higher temperatures than conventional steam turbines and requires a new design.[29] Possible corrosion effects in this piece of equipment should also be considered.[29] The combustor should be carefully analyzed as well, as it might show operational issues linked to stream recycling.[30] In addition, how the turbomachinery components are arranged in the Graz cycle is still being debated.[30]

## Outlook

According to the discussion in the preceding sections, the following comments can be made on the future directions of gas-CCS and the main challenges for achieving deployment at a commercial scale:

1. The potential contribution of CCS as a decarbonizing tool is now generally accepted, but costs are crucial for the wide-scale deployment of CCS and need to be reduced, through technology developments and knowledge transfer from demonstration – and then commercial-scale deployment. Strong policy drivers are also required to de-risk and create a favorable market for CCS and make it a reality.
2. Cost reduction is the ultimate driver of several process alternatives aimed at increasing the $CO_2$ partial pressure of the flue gas for natural gas combustion with post-combustion CCS systems. This can be achieved with a range of modifications to simple and combined cycle systems, as well as greater alterations through advanced gas turbine cycles, as explored herein. Demonstrating these technologies is not always easy and there is much ongoing work to scale-up these various methods to prove their functionality at a commercial level. Furthermore, gas-fired power plants are often employed as backup utilities and therefore, it is essential to analyze how flexibility will be affected because of their integration with the advanced configurations discussed in this work.
3. Supplementary firing is an already commercial-scale option that can be used to substantially increase the $CO_2$ content of the flue gas from NGCC power plants, especially if the additional fuel is burnt in sequential firing stages. Biomass can be used as supplementary fuel, leading to an additional reduction in the $CO_2$ emissions. The decrease in the overall plant efficiency is the main barrier associated with the implementation of supplementary firing. The use of NGCCs with supercritical steam cycles and/or in combination with EGR has been suggested to limit the efficiency reduction. However, further studies are required to analyze the implications this may have on the cost and flexibility of the system.
4. EGR and S-EGR are attractive options to increase the exhaust gas $CO_2$ concentration in NGCC power plants. The development of EGR has shown promising results, but there is a need to demonstrate and operate EGR at full plant scale. This would reduce the associated risks and facilitate knowledge transfer, which would change perceptions and attract industrial partners to invest in gas-CCS.
5. There is a limited amount of data relating to S-EGR configurations, therefore, it is difficult to quantify the advantages of this novel configuration. Investigating how S-EGR configurations influence the gas turbine and amine capture plant performance will be crucial to advancing this technology. There is a need to evaluate how actual exhaust gases affect S-EGR membrane performance. In addition, S-EGR membranes require optimization, where membrane choice, selectivity, permeability, size and cost will have an important role in the progress of this technology for commercial applications.
6. Humidification can bring about improved performances of both the energy and capture plants, where the improvements in performance tend to be more pronounced for HAT compared to STIG cycles. The amount of water required by these systems is substantial, as are the additional components needed, which add notably to their complexity and cost. Increases in the pressure ratio, often needed for humidified systems, also necessitate the use of higher-grade materials that are able to withstand the higher pressure. Whilst augmenting the $CO_2$ concentration of the flue gas with this method is obviously advantageous (up to $\sim$5%vol.), other methods of increasing this and decreasing the flue gas flowrate (and its $O_2$ content) appear more effective and cost efficient. Since CCS is generally not the main reason for humidification of gas turbine cycles, information on the improvements of $CO_2$ partial pressure in the flue gas are not widely reported.
7. Considerable effort is being devoted to making amine-based capture processes more economical through pilot scale and demonstration studies. In general, the issues to be addressed are more of a financial nature rather than technical, and work needs to be done to bring the costs down to acceptable levels and to optimize the flexible operation of gas-fired power plants with integrated capture systems. The PCC amine technology works and is currently being used at commercial scale on coal power plants. A high degree of knowledge transfer can be established between the Boundary Dam and Petra Nova commercial $CO_2$ capture

plants and future gas-CCS projects, which can assist in reducing costs and de-risking the deployment of gas-CCS. Moreover, there is a need for a first of a kind plant which can demonstrate the feasibility of post-combustion $CO_2$ capture in conjunction with a gas-fired power plant at commercial scale.

8. Oxy-fired gas cycles are a promising option to achieve nearly zero $CO_2$ emissions. High electrical efficiencies are reported for these systems, especially for the Allam (NET Power) and CES cycles. However, they are still under development and several technical barriers should be overcome before they are ready for commercialization, mainly related to the design of equipment suitable for the high temperatures and pressures of operation. Progress is being made, especially in the CES cycle through experimental testing. The current construction of a demonstration facility anticipates further advancements in the Allam (NET Power) cycle in the near future.

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